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AIR-LIKE DISCHARGES WITH CO_2, NO, NO_2, AND N_2O AS IMPURITIES

by

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June 1969

U.S. ARMY ABERDEEN RESEARCH AND DEVELOPMENT CENTER
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Signature and Propagation Laboratory

RDTE Project No. 1T061102B53

A B E R D E E N P R O V I N G G R O U N D, M A R Y L A N D

B A L L I S T I C R E S E A R C H L A B O R A T O R I E S

REPORT NO. 1437

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June 1969

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ABSTRACT

Computer solutions to 24 time-rate-of-change equations have been obtained for air-like discharges attainable in a laboratory facility designed for the study of reactions of ionospheric importance. The manner in which the solutions are affected by initial number densities of CO_2, NO, NO_2, and N_2O, corresponding to impurity levels of 0, 0.1, 10, and 1000 ppm, is presented. The effects of principal reactions on the number densities of detectable species are discussed. For the conditions specified in the computer program, the initial NO_2 density greatly affects the negative ion densities and the initial NO density greatly affects the observable positive ion densities.

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INTRODUCTION

Whenever air is subjected to ionization, the minor constituents (species other than molecular nitrogen and molecular oxygen) play a major role in determining the physical properties, such as composition and electrical conductivity, of the air. Considerable effort is being exerted toward understanding the role of each of the minor constituents in ionized air, especially in the ionosphere of the earth's atmosphere.

Minor constituents in air-like discharges come from three sources: (1) the air sample, (2) the experimental apparatus, and (3) the chemistry initiated by the discharge.

The normal composition of clean, dry atmospheric air near sea level is,[1†] in terms of percentage by volume, N_2 - 78.084, O_2 - 20.9476, A - 0.934, CO_2 - 0.0314*, Ne - 0.001818, He - 0.000524, Kr - 0.000114, Xe - 0.0000087, H_2 - 0.00005, CH_4 - 0.0002*, N_2O - 0.00005, O_3 - 0 to 0.000007*, SO_2 - 0 to 0.0001*, NO_2 - 0 to 0.000002*, NH_3 - 0 to trace*, CO - 0 to trace*, and I_2 - 0 to 0.000001*. The contents marked with an asterisk may undergo significant temporal and spatial variations relative to the values indicated. In addition, normal atmospheric air contains water in varying amounts. Research grade air is normally a 4:1 mixture of N_2 and O_2. Typical impurity concentrations in parts per million (ppm) are[2] A - 15, CO_2 - 0.5, CO - 1, He - 5, H_2 - 1, H_2O - <2, CH_4 - 1, N_2O - 0.1, C_2H_2 - 0.05, and total hydrocarbon - 1. The noble gases do not greatly affect the chemistry of air discharges, since the noble gas ions transfer their charge to N_2 or O_2 and the neutral noble gas species are relatively unreactive.

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†*References are listed on page* 62.

In regard to possible positive charge transfer reactions, a look at the ionization potentials of the aforenamed species, and other species of interest later on, is informative. The ionization potentials in electron volts (eV) are He - 24.580, Ne - 21.559, A - 15.759, N_2 - 15.580, H_2 - 15.425, N - 14.532, CO - 14.013, Kr - 13.996, CO_2 - 13.769, O - 13.618, CH_4 - 12.99, N_2O - 12.894, O_3 - 12.80, H_2O - 12.619, SO_2 - 12.34, Xe - 12.127, O_2 - 12.063, C_2H_2 - 11.40, NH_3 - 10.34, NO_2 - 9.78, I_2 - 9.41, and NO - 9.267. In exothermic charge transfer reactions the positive charge is transferred from the species with higher ionization potential to the species with lower ionization potential. For this reason, NO^+ has been called the "terminating positive ion" in ionized air. This title can be misleading since it has been shown[3,4,5] that NO and H_2O will cluster to NO^+ and that the clustered ions undergo reactions to create new ions.

The second class of minor constituents are those species which come from the walls of the container, the electrodes, the pumping system, and other places inside the experimental apparatus. The contribution to the minor constituents from these sources can be diminished, but not eliminated, by employment of careful experimental techniques.

A third source of minor constituents in air discharges is the chemistry which accompanies and follows the discharge. If air has been ionized, the number densities of the minor constituents are not the same as the number densities for the air prior to ionization. Sometimes the phrase, "single-pulse operation", has been used when the time between pulses is very much greater than the duration of the ionizing pulse. This method of ionization delays the build-up of the minor constituents but is not the same as starting with

air which has not been subjected to ionization. Rapid pulsing of the ionizing source does not significantly change the buildup of the minor constituents from that accompanying continuous ionization.[6]

A description of a laboratory facility for the study of reactions of ionospheric importance has recently been published.[7] This facility utilizes a spatially uniform flux of 1.5 MeV electrons to ionize the gas contained in a 120 cm i.d. reaction chamber. The ions effusing through an orifice at the wall are identified by means of a mass spectrometer. The electron density in the volume is measured by the change in resonant frequency and quality factor of the chamber employing standard microwave cavity techniques. The cavity is sufficiently large that for pressures above one Torr the charged species are predominantly lost by volume reactions. While understanding the reactions which occur in this large reaction chamber has been one of the principal motivations for the work presented here, the general description of the chemistry is applicable to other air-like discharges. For practical reasons the gas load in the cavity is not normally replaced after every pulse of ionization; therefore buildup of the minor neutral constituents occurs. This work will present the effects of different initial concentrations of CO_2, NO, NO_2, and N_2O on the chemistry of continuous discharges in air-like mixtures under specified conditions.

RATE EQUATIONS

If one desires to predict the number densities of the many possible species at any time during or after the ionization of air, one must know (1) the initial number densities of the species involved in the reactions, (2) the reactants and products of the reactions, (3) the reaction rate constant

for each reaction at the appropriate temperature, (4) the rate of production of each species by means other than reactions, (5) the loss processes and their rates for each species by means other than reactions, and (6) how to solve the several simultaneous time-rate-of-change equations (hereafter called rate equations), generally by using a computer program.

This work will consider the continuous ionization of an air-like mixture in the C. C. Dewey facility at a total pressure of 10.7 Torr and a temperature of 300 K. Because of the large reservoir of N_2 and O_2, the concentrations of these species will not be changed appreciably by the reactions. Therefore the concentrations of N_2 and O_2 are held constant in the computer program at 2.754×10^{17} cm^{-3} and 6.886×10^{16} cm^{-3}, respectively. The concentration of of water molecules depends greatly on the conditioning of the chamber and ancillary equipment prior to the addition of the gas as well as the gas composition itself. A crude estimate indicated a water impurity of 0.1 ppm.[8] The water molecules will undergo reaction, cluster to other species, and be adsorbed on the chamber walls. Very little is known quantitatively about these processes; therefore for this work the concentration of water molecules has been held constant at 3.443×10^{10} cm^{-3}.

Ionization and reactions create several species whose concentration may vary during the duration of the discharge. The following 24 species are treated as time-varying: electrons, NO_2^-, $NO_2^- \cdot H_2O$, NO_3^-, O^-, O_2^-, O_3^-, CO_3^-, N^+, N_2^+, NO^+, $NO^+ \cdot H_2O$, $NO^+ \cdot NO$, O^+, O_2^+, N, NO, NO_2, NO_3, N_2O, O, O_3, CO_2, and $O_2(^1\Delta)$. It is to be noted that three clustered ions, $NO_2^- \cdot H_2O$, $NO^+ \cdot H_2O$, and $NO^+ \cdot NO$ are considered; hence in the program NO_2^- and NO^+ are not terminating ions. The

only excited state species considered is $O_2(^1\Delta)$. As will be seen later, for the stated rates of production and reactions, $O_2(^1\Delta)$ is not very important.

Following a discharge the charged particle concentrations will approach zero with time. On the other hand, the neutral species will approach equilibrium concentrations which are not the same as those before the discharge. In order to investigate the importance of different impurity concentrations on the chemistry of air-like discharges, simultaneous rate equations were solved for the 24 time varying species with different initial number densities of CO_2, NO, NO_2, and N_2O. Solutions were obtained for four cases. For each case the concentrations of the time-invariant species, N_2, O_2, and H_2O, were not changed. Except as specified below, the initial number densities of the time-varying species were zero. For Case I, the initial number density of CO_2 was 3.443×10^{10} cm^{-3}. For Case II, the initial number densities of CO_2, NO, NO_2, and N_2O were 3.443×10^{10} cm^{-3} each. For Case III, the initial number densities of CO_2, NO, NO_2, and N_2O were 3.443×10^{12} cm^{-3} each. For Case IV, the initial number densities of CO_2, NO, NO_2, and N_2O were 3.443×10^{14} cm^{-3} each. Except for CO_2, Case I corresponds to an impurity concentration of 0 ppm. Cases II, III, and IV correspond to impurity concentrations of 0.1, 10, and 1000 ppm, respectively, for CO_2, NO, NO_2, and N_2O. Hirsh et al.[8] have estimated that the total concentration of impurities contributed by the system is less than 10 ppm. Minor constituents which are created by the chemistry may attain number densities exceeding 10^{12} cm^{-3}, the equivalent of 10 ppm.

The number densities of the species are linked together by reactions. Thus one must know the reactants, the rate constant, and the products for every reaction if a true picture of the chemistry of the discharge is to

be obtained. Unfortunately, complete information is not available. Nevertheless, many reactions have been studied and their rate constants determined. For this work 182 reactions were assigned rate constants. These are listed for a temperature of 300 K in the Appendix. Equivalent solutions could have been obtained with 50 selected reactions. The reactions are numbered in the Appendix according to their use in the computer program. The seemingly missing reactions were assigned a rate constant of zero. Most of the rate constants were obtained from the DASA Reaction Rate Handbook[9] without regard to the uncertainties listed there. The author has reservations about some of the rate constants and, if the calculations were repeated, certain rate constants would be changed. However, it is not the intent of this work to discuss the accuracy of rate constants.

For each of the time-varying species, an equation can be written in the form

$$d[n]/dt = q(n) + \sum \text{Populating Reaction Rates for Species n} - \nu(n)[n] - \sum \text{Depopulating Reaction Rates for Species n,} \quad (1)$$

where [n] denotes the number density of species n, q(n) is the rate of production of species n by means other than reactions, and $\nu(n)$ is the loss frequency of species n by means other than reactions, e.g., diffusion.

The rate of ionization for air-like mixtures in the G. C. Dewey facility has been determined. The rate is proportional to the beam current density and gas pressure. Ionization is produced by both the primary electron beam and the secondary electrons. In addition to direct ionization, the energetic electrons will produce dissociative ionization and excitation at rates which have not been determined. For this work we will assume that 20 percent of the

total ionization is dissociative for both N_2 and O_2. (Dalgarno[10] has made the same assumption.) We will further assume that the rate of production of $O_2(^1\Delta)$ is the same as the rate of production of O_2^+. We will neglect multiple ionization and dissociation without ionization. The rates of production employed in the program are as follows:

$$q(N_2^+) = 2.24 \times 10^{10} \text{ cm}^{-3} \text{ sec}^{-1}$$
$$q(O_2^+) = 5.01 \times 10^{9} \text{ cm}^{-3} \text{ sec}^{-1}$$
$$q(N^+) = 5.60 \times 10^{9} \text{ cm}^{-3} \text{ sec}^{-1}$$
$$q(O^+) = 1.25 \times 10^{9} \text{ cm}^{-3} \text{ sec}^{-1}$$
$$q(e) = 3.43 \times 10^{10} \text{ cm}^{-3} \text{ sec}^{-1}$$
$$q(N) = 5.60 \times 10^{9} \text{ cm}^{-3} \text{ sec}^{-1}$$
$$q(O) = 1.25 \times 10^{9} \text{ cm}^{-3} \text{ sec}^{-1}$$
$$q(O_2(^1\Delta)) = 5.01 \times 10^{9} \text{ cm}^{-3} \text{ sec}^{-1}$$

These rates of production reflect the experimental observation that the efficiency for ionization of N_2^+ and O_2^+ are not exactly equal.

For the G. C. Dewey facility, the diffusive loss frequency of the electron density, $\nu(e)$, at a pressure of 10.7 Torr is 0.065 sec^{-1}. For pressures above one Torr, the loss frequency by diffusion has been found to be negligible compared to the loss frequency by reactions. Since for this work $\nu(n)$ is unimportant, the charged species were arbitrarily assigned the same loss frequency as the electrons and the loss frequency for each neutral species was set to zero.

The solutions to the 24 simultaneous equations of the form of Eq. (1) have been obtained using a modified version of the computer programs developed by Keneshea.[11] The solutions are given as number densities for each of the 24

species at known times. The number density of a species at a particular time is determined from the simultaneous solution of the differential equations unless the species has reached a state of quasi-equilibrium. Once a species has reached quasi-equilibrium, the number density is determined from the algebraic equations. This procedure is repeated for every species except the largest positive ion (or the largest negative ion, the choice depending on the option selected). The largest positive ion density (or largest negative ion density) is computed from charge balance. The time step in the computer program is increased and the number densities recalculated from the differential and algebraic equations.

SOLUTIONS

Solutions to the rate equations were obtained for the four cases of different initial number densities of CO_2, NO, NO_2, and N_2O for continuous ionization with a duration of at least 10^4 s. Since the time step in the calculations is not fixed but is controlled by the computer program, number densities for all cases were not calculated at exactly the same time. However, the difference is not enough to hinder a comparison. Cases II and III, corresponding to 0.1 and 10 ppm impurity levels, respectively, are realistic cases. A comparison of the solutions for these cases yields information about what can be expected to occur during air-like discharges. Case I is not attainable and Case IV requires the deliberate addition of CO_2, NO, NO_2, and N_2O.

Tables I, II, and III give the number densities for the 24 time-varying species near 10^{-6} and 10^{-3} s, 1 and 10 s, and 100 and 1000 s, respectively,

after the initiation of continuous ionization for the four cases. The number densities of the time-invariant species, N_2, O_2, and H_2O, are 2.754×10^{17}, 6.886×10^{16}, and 3.443×10^{10} cm^{-3}, respectively. The times at which the number densities listed in the tables were computed are in seconds as indicated:

Case I	1.11(-6)	1.08(-3)	1.05	10.6	116	1.00(3)
Case II	1.11(-6)	1.08(-3)	1.02	12.2	125	1.12(3)
Case III	1.11(-6)	1.08(-3)	1.02	14.7	136	1.30(3)
Case IV	1.11(-6)	1.06(-3)	1.02	14.4	135	1.21(3)

(The quantity enclosed by parenthesis is the power to which ten is raised.)

In order to follow the variation in number density of a particular species with duration of ionization in the G. C. Dewey facility, the species must be detectable, i.e., charged and with a sufficient concentration. The electron density is measured by employing microwave cavity techniques. Positive and negative ions are identified and monitored by means of a mass spectrometer. At present, the ground state neutral species are not monitored.

At 10^{-6} s, the electron and O_2^+ densities are on the borderline of detectability. At this time neither is very dependent on the impurity concentrations. It can be noted that N^+ and N_2^+ have already reached equilibrium. At 10^{-3} s, more species are detectable. The electron density decreases as the NO_2 density increases. The dominant negative ion switches between Case II and Case III from O_2^- to NO_2^-. The dominant positive ion switches between Case II and Case III from O_2^+ to NO^+. The switching of the dominant positive and negative ions between 0.1 and 10 ppm impurity levels illustrates vividly the importance of knowing the initial number densities of the minor constituents of air-like discharges.

The solutions were plotted semi-logarithmically for times up to 300 s. The solutions for the electron density are given in Figure 1. The decrease in the electron density for Case IV is attributable to the attachment of electrons to NO_2. The corresponding increase in the NO_2^- density is shown in Figure 2.

The structures shown on Figure 2 for Cases I, II, and III are significant. The decrease in NO_2^- density for Case III follows the decrease in NO_2 density. The NO_2 solutions are shown in Figure 3. As can be seen from Table IV, the principal depopulating reactions for Case III during the time interval 1 - 300 s for NO_2 are Reactions 95, 151, and 157. (Principal reactions are defined as those which contribute at least 10 percent to the total rate at the specified time and are the only reactions listed in the tables.) Reaction 95 is the negative charge transfer of O_2^- with NO_2 yielding NO_2^- and O_2. Reaction 151 is the neutral rearrangement of NO_2 with O yielding NO and O_2, and Reaction 157 is the neutral rearrangement of NO_2 with N yielding N_2 and O_2. (Reaction 157 is effectively a sink for the minor constituents since the N_2 and O_2 are held constant; however, the branching indicated by the rate constants assigned to Reactions 157, 158, and 159 is not in agreement with that observed by Phillips and Schiff.[12] They found that Reaction 158 is the most likely.) As shown in Table V, the dominant populating reaction for NO_2 during the time interval shown on Figure 3 changes from Reaction 56, the mutual neutralization of NO_2^- and NO^+, to Reaction 160, the neutral rearrangement of NO and O_3.

Atomic nitrogen and atomic oxygen are the keys to the NO_2 and NO_2^- densities. Figures 4 and 5 show that the atomic nitrogen and atomic oxygen densities, respectively, increase as the NO_2 density decreases. Tables VI and VII

list the major populating and depopulating rates, respectively, for atomic nitrogen. The importance of mutual neutralization with rearrangement as a source of atomic nitrogen is shown by the rates for Reactions 69, 77, 179, and 180. Very little is known about mutual neutralization and even less is known about mutual neutralization with rearrangement. Consequently the rate constants assigned to reactions of this type are estimated values. Theoretical calculations by Chan[13] yield 1.14×10^{-7} cm^3 sec^{-1} at 300 K for Reaction 79 and indicate that dissociation is the preferred channel for mutual neutralization. Reactions 155 and 156 produce atomic oxygen. Reaction 157 connects the atomic nitrogen density to the NO_2 density. As the NO_2 density decreases, the N density increases for Case III.

Tables VIII and IX give the major populating and depopulating rates, respectively, for atomic oxygen. The rates for Reactions 69, 77, 79, 81, 82, and 179 indicate the importance of mutual neutralization to the production of atomic oxygen. Table VIII shows that reactions are the principal source of atomic oxygen. Table IX shows that the loss of atomic oxygen is primarily by three-body neutral recombination with O_2, Reactions 138 and 139, to produce O_3 until the density of NO_2 is sufficiently large that Reaction 151 predominates. When the NO_2 density is large, as in Case IV, O_3 does not build up. This is shown in Figure 6.

The NO_2^- density naturally depends on the NO_2 density. Tables X and XI list the principal populating and depopulating rates, respectively, for NO_2^-. At early times O_2^- charge transfers with NO_2 via Reaction 95 to produce NO_2^-. Table X shows that for Cases I, II, and III the charge transfer of O_3^- with NO_2 is important; however, for Case IV the O_3^- density is not sufficient for

Reaction 98 to be important. On the other hand, only for Case IV is the three-body electron attachment to NO_2, Reaction 28, important.

As shown by Figure 3, the NO_2 density goes through a minimum and then steadily increases. Not shown by Figure 3 is the fact that the NO_2 density in Case III also goes through a minimum and then steadily increases. The NO_2^- density follows the NO_2 density until the production of NO_3^- via Reactions 175 and 212 occurs. The species responsible for changing the dependence of NO_2^- on NO_2 is O_3. Both Reactions 160 and 212 require O_3. In turn, the O_3 density depends on the O density. For Case I the initial buildup of the NO_2 density is caused by Reaction 14, the associative detachment of O_2^- by N. The buildup of the NO_2^- density in Figure 2 mostly reflects the buildup of the NO_2 density and to a lesser extent the buildup of NO and CO_3^-. The latter produces NO_2^- via Reaction 210. Comparison of Tables X and XI with Tables IV and V reveals the interconnection between the populating and depopulating reactions for NO_2 and NO_2^-.

The initial step in the negative ion chemistry is the formation of O_2^- via three-body attachment, Reactions 24 and 25. Since N_2 and O_2 are time invariant, the time variation of the rate of production follows the time variation of the electron density. As seen in Figure 1, the electron density is nearly constant in time. Therefore the change in O_2^- density with time shown in Figure 7 is caused by changes in the depopulating reaction rates. The decrease in O_2^- density for Cases I and II reflects the buildup of O_3 so that Reaction 96 becomes the dominant depopulating reaction. The depopulating rates are given in Table XII. The increase in O_2^- density for Case III reflects the decrease in NO_2 density as shown in Figure 3 for this case.

Negative charge transfer of O_2^- with O_3 via Reaction 96 produces O_3^-. Since the other populating reactions are much smaller, the productions of O_3^- depends on the number density of O_3. The O_3^- density is shown in Figure 8. For Case IV, the O_3 density is not built up and hence the O_3^- density is very small. For Case III, the O_3^- density is small, but increasing. For Cases I and II, the O_3^- density reaches a maximum and then decreases as the NO_2 and NO_3 densities increase. Table XIII gives the O_3^- depopulating rates. The early loss of O_3^- in Cases I and II is by mutual neutralization.

As shown by Figure 9, the CO_3^- density follows the O_3^- density. The negative charge transfer of O_3^- with CO_2, Reaction 208, populates CO_3^-. Depopulation occurs through negative charge transfer of CO_3^- with NO and NO_2, Reactions 210 and 211, respectively.

For Cases I, II, and III, NO_3^- becomes the dominant negative ion. However, because of the smaller O_3 density in Case IV and the effects of the smaller O_3 density, the NO_3^- density is smaller in Case IV than in the other cases as shown in Figure 10. The major populating rates for NO_3^- are given in Table XIV. The only depopulating process for NO_3^- included in the computer program is mutual neutralization, with and without rearrangement.

The importance of O_3 to several of the negative ions has been mentioned. This importance can be summarized readily by examining the negative ion formation reactions. The attachment reactions are:

24. $e + O_2 + O_2 \rightarrow O_2^- + O_2$

25. $e + O_2 + N_2 \rightarrow O_2^- + N_2$

28. $e + NO_2 + N_2 \rightarrow NO_2^- + N_2$

Reaction 28 is important for Case IV only. Once O_2^- is formed, it creates other negative ions via:

$$95.\quad O_2^- + NO_2 \rightarrow O_2 + NO_2^-$$

$$96.\quad O_2^- + O_3 \rightarrow O_2 + O_3^-$$

$$173.\quad O_2^- + NO_3 \rightarrow O_2 + NO_3^-$$

Once O_3^- is formed, it creates other negative ions via:

$$98.\quad O_3^- + NO_2 \rightarrow O_3 + NO_2^-$$

$$174.\quad O_3^- + NO_3 \rightarrow O_3 + NO_3^-$$

$$208.\quad O_3^- + CO_2 \rightarrow O_2 + CO_3^-$$

Once CO_3^- is formed, it creates other negative ions via:

$$210.\quad CO_3^- + NO \rightarrow CO_2 + NO_2^-$$

$$211.\quad CO_3^- + NO_2 \rightarrow CO_2 + NO_3^-$$

Once NO_2^- is formed, it creates NO_3^- via:

$$175.\quad NO_2^- + NO_3 \rightarrow NO_2 + NO_3^-$$

$$212.\quad NO_2^- + O_3 \rightarrow O_2 + NO_3^-$$

Now let's examine the rolls that O_3 plays. If the O_3 density is small, Reaction 96 is unimportant; hence O_3^- is not produced. If O_3^- is not produced, Reactions 98, 174, and 208 are unimportant. If Reaction 208 is unimportant, CO_3^- is not produced. If CO_3^- is not produced, Reactions 210 and 211 are unimportant. In Case IV this is the situation. Why? The O_3 density is mainly populated by Reactions 138 and 139, three-body recombination of atomic oxygen and molecular oxygen. When a large reservoir of NO_2 exists as in Case IV, the atomic oxygen is lost by reaction with NO_2, Reaction 151, and hence is not available to form O_3. In addition, the only reaction populating NO_3 which

does not involve the NO_3^- ion is Reaction 172 and Reaction 172 involves O_3. Consequently, for Case IV the important negative ion formation reactions are limited to Reactions 24, 25, 28, and 95. On the other hand, if the O_3 density is large, Reaction 160 will produce NO_2 and the preceding reactions produce the principal negative ions observable in an air-like discharge.

Are NO_2^- and NO_3^- terminal negative ions in air-like discharges? No. NO_2^- has been found to cluster with H_2O and HNO_2.[14] Many complex negative ions have been observed. Water is always present to some extent in air-like discharges, and HNO_2 is produced by chemical reactions.[3] The loss processes for the complex clustered ions have not been completely identified. The computer program has assumed mutual neutralization as the loss process for $NO_2^- \cdot H_2O$. Figure 11 shows the solutions for $NO_2^- \cdot H_2O$. The general structural characteristics of the solutions follow those of NO_2^-.

Ionization of air-like mixtures produces the positive ions, N^+, N_2^+, O^+, and O_2^+, from the major constituents, N_2 and O_2. Ionization of minor constituents is negligible. Table I reveals that the N^+ density reaches equilibrium very early. The N^+ ions produced by the ionization are lost by Reactions 185 and 190. Both reactions involve O_2, a time-invariant species. Therefore, from the time the N^+ density reaches equilibrium, it does not change. Similar statements can be made about N_2^+ and O^+. The N_2^+ ions produced by the ionization are lost by charge transfer to O_2, Reaction 89. From the time the N_2^+ density reaches equilibrium, it does not change. The O^+ ions produced by the ionization are lost by charge transfer to O_2, Reaction 83, and charge rearrangement with N_2, Reaction 116. The charge transfer reactions, along with $q(O_2^+)$, make the rate of population for O_2^+ nearly the same as the rate of ionization. The O_2^+ depopulating rates are given in Table XV. It is seen that the initial

number density of NO greatly affects the loss of O_2^+ via Reaction 87. The solutions show the dependence of the O_2^+ density on the NO density. Figures 12 and 13 give the solutions for O_2^+ and NO, respectively. The Case III solutions indicate clearly that the O_2^+ density increases as the NO density decreases. The Case IV solutions show that the O_2^+ density is small when the NO density is large. One would think from this that the NO^+ density would be large for Case IV. Figure 14 shows that this is not the case. The NO^+ ions cluster with the NO molecule via Reaction 199 to form the $NO^+ \cdot NO$ dimer ion. Comparison of Figures 13 and 15 reveals the similarity of the $NO^+ \cdot NO$ solutions to those for NO. The major populating rates for NO^+ are listed in Table XVI and the depopulating rates are listed in Table XVII. (The O_2^+ ions will cluster with O_2 to form the O_4^+ dimer ion; however, this process has not been included in these calculations.)

In the computer program the dimer ions are depopulated by mutual neutralization. In reality, the $NO^+ \cdot NO$ ions react with H_2O to form $NO^+ \cdot H_2O$.[3] $NO^+ \cdot H_2O$ may add one or two more water molecules. The multi-water-clustered NO^+ ions react or dissociate to produce multi-water-clustered H_3O^+ ions either directly or through addition clustering.

The positive ion formation mechanisms down to the original dimer ions are fairly simple. Ionization produces N^+, N_2^+, O^+, and O_2^+. The following reactions lead to the dimer ions:

185. $N^+ + O_2 \rightarrow N + O_2^+$

190. $N^+ + O_2 \rightarrow O + NO^+$

89. $N_2^+ + O_2 \rightarrow N_2 + O_2^+$

83. $O^+ + O_2 \rightarrow O + O_2^+$

116. $O^+ + N_2 \rightarrow N + NO^+$

87. $O_2^+ + NO \rightarrow O_2 + NO^+$

119. $O_2^+ + N_2 \rightarrow NO + NO^+$

198. $NO^+ + H_2O + M \rightarrow NO^+ \cdot H_2O + M$

199. $NO^+ + NO + M \rightarrow NO^+ \cdot NO + M$

As shown by Figure 16, the solutions for $O_2(^1\Delta)$ are not greatly affected by the initial number densities of the four cases. Under the conditions for which these calculations were made, $O_2(^1\Delta)$ is not an important species.

For the initial number densities of Case II, a study was made of the changes in the solutions effected by increasing or decreasing all positive ion-negative ion reaction rate constants by an order of magnitude. For times greater than approximately 10 s, the solutions for all the neutral species are within a factor of two of the solutions obtained using the rate constants given in Appendix I. For electrons N^+, N_2^+, and O^+ the solutions are essentially unchanged. For the remaining charged particle species, large changes in the solutions resulted, sometimes exceeding an order of magnitude for NO_3^-, $NO_2^- \cdot H_2O$, $NO^+ \cdot H_2O$, and $NO^+ \cdot NO$.

A note of caution is now appropriate. The preceding discussion only partially explains the chemistry occurring in air-like discharges. Ionic species have been detected in air-like discharges which are not included in the program. In order to explain their appearance several more reactions will have to be included in the program. Furthermore, several values for important rate constants have been estimated, since neither experimental nor theoretical values exist. In any case, the gross chemistry of air-like discharges and the role of impurities are expected to remain generally as described.

CONCLUSIONS

Solutions of 24 time-rate-of-change equations during the continuous ionization of air-like mixtures for four sets of initial concentrations of CO_2, NO, NO_2, and N_2O have demonstrated the importance of knowing the initial concentrations of minor constituents. The initial N_2O densities did not affect the solutions. The initial CO_2 densities are not very important to the solutions. The CO_3^- solutions are influenced by the O_3 density. The O_3 density is affected by the NO_2 density. The initial NO_2 density greatly affects the reactions forming the negative ions. The initial NO density greatly affects the observable positive ion densities. While the solutions were obtained for the G. C. Dewey laboratory facility, similar effects on the charged particles in the upper atmosphere can be expected for various densities of NO and NO_2. Hence measurements of the NO density and the NO_2 density should accompany charged particle measurements in the upper atmosphere.

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TABLE I

NUMBER DENSITIES FOR CASES I, II, III, AND IV NEAR 10^{-6} AND 10^{-3} SECONDS

(Units of cm^{-3})

	$t = 10^{-6}$ s				$t = 10^{-3}$ s			
Species	I	II	III	IV	I	II	III	IV
e	3.8(4)*	3.8(4)	3.8(4)	3.6(4)	3.1(6)	3.1(6)	2.9(6)	3.6(5)
NO_2^-	1.1(-11)	1.8(- 1)	1.8(1)	1.7(3)	3.7(- 1)	1.0(6)	2.9(7)	3.6(7)
NO_3^-	2.0(-30)	4.3(-20)	4.6(-17)	3.7(-13)	7.3(-10)	3.7(-4)	5.8(-2)	9.8(-2)
O^-	5.6(-12)	5.6(-12)	5.6(-12)	6.0(-12)	3.8(- 2)	3.6(-2)	5.7(-3)	1.9(-6)
O_2^-	2.3(2)	2.3(2)	2.3(2)	1.8(2)	3.4(7)	3.3(7)	5.1(6)	6.4(3)
O_3^-	6.6(-14)	6.6(-14)	7.7(-14)	8.8(-13)	7.4(- 1)	7.4(-1)	1.7(-1)	3.1(-6)
CO_3^-	1.8(-19)	1.8(-19)	2.1(-17)	2.3(-14)	2.5(- 3)	2.5(-3)	7.6(-2)	1.4(-5)
$NO_2^- \cdot H_2O$	3.6(-18)	7.9(- 8)	7.9(- 6)	7.7(- 4)	1.2(- 4)	4.2(2)	1.5(4)	2.2(4)
N^+	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)
N_2^+	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)
NO^+	3.2(3)	3.2(3)	3.3(3)	7.8(3)	3.7(6)	4.2(6)	2.6(7)	2.8(7)
$NO^+ \cdot H_2O$	4.1(- 3)	4.1(- 3)	4.2(- 3)	8.2(- 3)	4.6(3)	5.0(3)	2.8(4)	3.8(4)
$NO^+ \cdot NO$	1.0(-14)	8.3(- 5)	8.3(- 3)	1.6(0)	7.4(- 4)	1.0(2)	5.5(4)	7.6(6)
O^+	6.4(2)	6.4(2)	6.4(2)	6.4(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)
O_2^+	3.3(4)	3.3(4)	3.3(4)	2.8(4)	3.3(7)	3.3(7)	1.1(7)	1.1(5)
N	9.4(3)	9.4(3)	9.4(3)	9.4(3)	9.3(6)	9.3(6)	8.7(6)	6.3(5)
NO	6.6(0)	3.4(10)	3.4(12)	3.4(14)	5.4(5)	3.4(10)	3.4(12)	3.4(14)
NO_2	1.9(-10)	3.4(10)	3.4(12)	3.4(14)	3.2(1)	3.4(10)	3.4(12)	3.4(14)
NO_3	7.5(-35)	3.6(-14)	5.4(-11)	4.7(- 7)	4.3(-13)	4.0(-5)	3.3(-2)	5.5(0)
N_2O	3.6(-13)	3.4(10)	3.4(12)	3.4(14)	1.1(- 6)	3.4(10)	3.4(12)	3.4(14)
O	5.1(3)	5.1(3)	5.1(3)	5.1(3)	5.6(6)	5.6(6)	5.9(6)	5.1(6)
O_3	3.6(- 2)	4.1(- 2)	6.3(- 1)	5.3(1)	3.9(4)	4.5(4)	3.2(5)	4.4(5)
CO_2	3.4(10)	3.4(10)	3.4(12)	3.4(14)	3.4(10)	3.4(10)	3.4(12)	3.4(14)
$O_2(^1\Delta)$	5.6(3)	5.6(3)	5.6(3)	5.6(3)	5.4(6)	5.4(6)	5.4(6)	5.3(6)

*The quantity enclosed by parenthesis is the power to which ten is raised. The number densities were calculated to four significant figures. Accuracy to more than one significant figure is not justified, but two figures are given to show trends better.

TABLE II

NUMBER DENSITIES FOR CASES I, II, III, AND IV NEAR 1 AND 10 SECONDS

(Units of cm^{-3})

	t = 1 s				t = 10 s			
Species	I	II	III	IV	I	II	III	IV
e	3.2(6)*	3.2(6)	2.9(6)	3.6(5)	3.3(6)	3.3(6)	2.9(6)	3.6(5)
NO_2^-	7.3(5)	1.0(8)	3.4(8)	5.2(8)	9.2(6)	3.6(7)	3.2(8)	5.2(8)
NO_3^-	9.7(4)	2.9(6)	9.3(5)	2.9(4)	3.1(6)	1.5(7)	2.2(7)	2.4(5)
O^-	1.2(2)	9.5(1)	2.9(0)	2.7(-4)	1.2(2)	1.3(2)	2.4(1)	2.7(-4)
O_2^-	2.2(8)	1.7(8)	5.0(6)	6.4(3)	9.3(7)	9.3(7)	5.4(6)	6.4(3)
O_3^-	2.0(7)	1.4(7)	6.2(3)	7.8(-4)	6.5(7)	8.6(7)	7.9(4)	7.9(-4)
CO_3^-	1.4(8)	4.1(7)	2.8(4)	3.5(-3)	4.4(8)	2.3(8)	3.8(5)	3.5(-3)
$NO_2^- \cdot H_2O$	2.2(4)	3.6(6)	1.1(7)	1.2(7)	1.7(5)	9.2(5)	1.0(7)	1.2(7)
N^+	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)
N_2^+	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)
NO^+	1.4(8)	1.5(8)	2.9(8)	5.4(7)	4.1(8)	3.1(8)	2.9(8)	5.4(7)
$NO^+ \cdot H_2O$	1.2(7)	1.1(7)	1.8(7)	2.4(6)	4.8(7)	2.7(7)	1.8(7)	2.4(6)
$NO^+ \cdot NO$	1.4(5)	3.0(5)	3.5(7)	4.8(8)	3.8(6)	2.4(6)	3.4(7)	4.8(8)
O^+	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)
O_2^+	2.3(8)	1.8(8)	1.1(7)	1.1(5)	1.5(8)	1.3(8)	1.1(7)	1.1(5)
N	1.9(9)	1.7(9)	1.3(8)	8.3(5)	1.7(9)	1.6(9)	1.4(8)	8.3(5)
NO	2.2(10)	5.2(10)	3.4(12)	3.4(14)	1.5(11)	1.7(11)	3.4(12)	3.4(14)
NO_2	1.4(8)	3.3(10)	3.4(12)	3.4(14)	5.1(9)	2.1(10)	3.1(12)	3.4(14)
NO_3	2.1(6)	7.2(7)	4.1(7)	3.0(6)	1.3(9)	7.2(9)	7.6(9)	5.4(7)
N_2O	1.7(4)	3.4(10)	3.4(12)	3.4(14)	5.3(6)	3.5(10)	3.4(12)	3.4(14)
O	2.5(9)	2.5(9)	9.6(8)	9.1(6)	2.6(9)	2.6(9)	1.0(9)	9.1(6)
O_3	2.9(10)	2.9(10)	1.2(10)	1.1(8)	3.4(11)	3.9(11)	1.4(11)	1.2(8)
CO_2	3.4(10)	3.4(10)	3.4(12)	3.4(14)	3.4(10)	3.2(10)	3.4(12)	3.4(14)
$O_2(^1\Delta)$	5.0(9)	4.9(9)	5.0(9)	1.4(11)	2.8(10)	2.9(10)	5.6(10)	5.7(10)

*The quantity enclosed by parenthesis is the power to which ten is raised. The number densities were calculated to four significant figures. Accuracy to more than one significant figure is not justified, but two figures are given to show trends better.

TABLE III

NUMBER DENSITIES FOR CASES I, II, III, AND IV NEAR 10^2 AND 10^3 SECONDS

(Units of cm^{-3})

	$t = 10^2$ s				$t = 10^3$ s			
Species	I	II	III	IV	I	II	III	IV
e	3.2(6)*	3.2(6)	3.1(6)	3.6(5)	3.1(6)	3.1(6)	3.1(6)	3.8(5)
NO_2^-	3.3(7)	3.3(7)	1.4(8)	5.2(8)	6.5(6)	5.0(6)	8.1(5)	5.2(8)
NO_3^-	1.8(8)	2.1(8)	1.9(8)	2.0(6)	3.8(8)	3.8(8)	3.2(8)	5.3(6)
O^-	6.6(2)	7.1(2)	9.4(1)	2.7(-4)	2.6(3)	2.6(3)	2.6(3)	2.8(-4)
O_2^-	1.9(7)	1.7(7)	8.7(6)	6.4(3)	3.7(6)	3.5(6)	3.0(6)	7.2(3)
O_3^-	8.5(7)	7.6(7)	6.0(5)	8.0(-4)	1.5(7)	1.0(7)	3.4(6)	8.5(-4)
CO_3^-	9.2(7)	5.2(7)	5.1(6)	3.6(-3)	4.8(6)	1.9(6)	1.5(8)	4.0(-3)
$NO_2^- \cdot H_2O$	9.7(5)	9.9(5)	4.8(6)	1.2(7)	1.9(5)	1.5(5)	1.9(4)	1.1(7)
N^+	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)	8.1(1)
N_2^+	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)	1.6(3)
NO^+	2.6(8)	2.5(8)	3.0(8)	5.4(7)	2.0(8)	2.0(8)	2.5(8)	5.3(7)
$NO^+ \cdot H_2O$	1.8(7)	1.6(7)	1.9(7)	2.4(6)	1.1(7)	1.1(7)	1.7(7)	2.3(6)
$NO^+ \cdot NO$	1.7(6)	1.6(6)	2.0(7)	4.8(8)	5.9(5)	6.5(5)	8.8(5)	4.8(8)
O^+	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)	7.6(2)
O_2^+	1.3(8)	1.3(8)	1.9(7)	1.1(5)	2.0(8)	1.9(8)	2.2(8)	1.1(5)
N	1.5(9)	1.4(9)	2.3(8)	8.3(5)	9.1(8)	8.1(8)	1.1(9)	8.3(5)
NO	1.8(11)	1.8(11)	2.0(12)	3.5(14)	9.7(10)	1.0(11)	9.6(10)	3.6(14)
NO_2	9.7(10)	1.2(11)	1.8(12)	3.4(14)	5.7(11)	6.9(11)	3.9(11)	3.2(14)
NO_3	2.0(11)	2.5(11)	2.1(11)	4.8(8)	2.3(12)	3.1(12)	7.5(12)	1.3(9)
N_2O	1.3(9)	3.6(10)	3.5(12)	3.4(14)	5.4(10)	1.0(11)	3.5(12)	3.4(14)
O	2.8(9)	2.8(9)	1.4(9)	9.2(6)	2.5(9)	2.3(9)	2.7(9)	9.8(6)
O_3	3.3(12)	3.6(12)	5.0(11)	1.1(8)	1.6(13)	1.6(13)	1.6(13)	1.1(8)
CO_2	2.6(10)	1.9(10)	3.4(12)	3.4(14)	3.8(10)	2.6(10)	3.5(12)	3.4(14)
$O_2(^1\Delta)$	7.6(10)	7.7(10)	1.1(11)	1.4(11)	7.0(10)	7.1(10)	7.1(10)	1.4(11)

*The quantity enclosed by parenthesis is the power to which ten is raised. The number densities were calculated to four significant figures. Accuracy to more than one significant figure is not justified, but two figures are given to show trends better.

TABLE IV

NO_2 DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
95		2.3(6)*	8.5(8)	3.9(9)	2.0(9)	1.2(10)	3.6(9)	4.4(9)
98			2.3(8)	5.8(9)			1.3(9)	5.0(9)
151				6.4(9)				7.3(9)
157				7.8(9)				
158								8.4(9)
211		1.2(6)	1.2(9)					

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
28	2.2(9)				2.8(10)	2.7(10)	2.7(10)	2.7(10)
95	3.2(10)	3.1(10)	3.0(10)	2.1(9)				
151		1.4(10)	1.4(10)	4.7(9)	7.8(9)	1.4(10)	1.4(10)	1.4(10)
157		6.8(9)	6.5(9)	6.6(9)				

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE V

NO_2 POPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
14	9.4(4)*	7.5(7)						
48			2.8(8)		6.8(6)	4.6(9)	9.5(8)	
56			7.6(8)			3.0(9)	2.2(9)	
81					3.4(6)	2.3(9)		
160			6.3(8)	2.0(10)			8.1(8)	2.1(10)
175				7.5(9)				7.9(9)
179			3.4(8)			1.5(9)	1.1(9)	

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
48	6.1(7)							
56	1.5(8)	2.0(10)	1.9(10)		2.0(8)	5.6(9)	5.6(9)	5.5(9)
72						2.4(10)	2.5(10)	2.5(10)
144					4.8(7)			
160			5.9(9)	1.9(10)				
175				3.0(9)				
179	7.6(7)	9.9(9)	9.3(9)		1.0(8)			

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE VI

N POPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
q(N)	5.6(9)*	5.6(9)	5.6(9)	5.6(9)	5.6(9)	5.6(9)	5.6(9)	5.6(9)
69				7.6(9)				7.8(9)
77		2.4(9)	3.8(9)			2.3(9)	2.8(9)	
179						1.5(9)	1.1(9)	
180			2.7(9)				2.6(9)	
185	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
q(N)	5.6(9)	5.6(9)	5.6(9)	5.6(9)	5.6(9)	5.6(9)	5.6(9)	5.6(9)
69				7.9(9)				
179		9.9(9)	9.3(9)			2.8(9)	2.8(9)	2.7(9)
185	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE VII

N DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
155	5.5(7)*	5.0(9)	1.0(10)	5.4(9)	5.5(7)	5.3(9)	9.4(9)	4.8(9)
156			5.7(9)	1.9(9)	7.0(6)	6.9(8)	5.9(9)	1.8(9)
157				7.8(9)				8.4(9)
Reaction Number	**Case III Rates at 1.08(-3)s**	**1.02(-1)s**	**1.47(1)s**	**1.30(3)s**	**Case IV Rates at 1.06(-3)s**	**1.30(-1)s**	**1.44(1)s**	**1.21(3)s**
155				6.8(9)				
156	6.6(8)	1.0(10)	1.0(10)	2.4(9)	4.8(9)	6.3(9)	6.3(9)	6.5(9)
157	4.5(8)	6.8(9)	6.5(9)	6.6(9)	3.3(9)	4.3(9)	4.3(9)	4.0(9)

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE VIII

O POPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
q(0)	1.3(9)*	1.3(9)	1.3(9)	1.3(9)	1.3(9)	1.3(9)	1.3(9)	1.3(9)
69				7.6(9)				7.8(9)
77		2.4(9)	3.8(9)			2.3(9)		
79		6.5(9)				3.5(9)		
81						2.3(9)		
82				7.5(9)				7.3(9)
83	1.1(9)				1.1(9)			
155		5.0(9)	1.0(10)	5.4(9)		5.3(9)	9.4(9)	4.8(9)
156			5.7(9)				5.9(9)	
190	2.8(9)	2.8(9)			2.8(9)	2.8(9)		

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
q(0)	1.3(9)	1.3(9)	1.3(9)	1.3(9)	1.3(9)	1.3(9)	1.3(9)	1.3(9)
69				7.9(9)				
82				7.0(9)				
83	1.1(9)				1.0(9)			
155				6.8(9)				
156	6.6(8)	1.0(10)	1.0(10)		4.8(9)	6.3(9)	6.3(9)	6.5(9)
179		9.9(9)	9.3(9)			2.8(9)	2.8(9)	2.7(9)
190	2.8(9)	2.8(9)	2.8(9)		2.8(9)	2.8(9)	2.8(9)	2.8(9)

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE IX

) DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
138	1.5(7)*	3.5(9)	6.8(9)	6.5(9)	1.5(7)	3.6(9)	6.8(9)	6.1(9)
139	5.9(7)	1.4(10)	2.7(10)	2.6(10)	5.9(7)	1.4(10)	2.7(10)	2.4(10)
151				6.4(9)				7.3(9)

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
138			2.7(9)	7.0(9)				
139	6.2(7)	9.2(9)	1.1(10)	2.8(10)				
151	9.1(7)	1.4(10)	1.4(10)	4.7(9)	7.8(9)	1.4(10)	1.4(10)	1.4(10)

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE X

NO_2^- POPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
95		2.3(6)*	8.5(8)	3.9(9)	2.0(9)	1.2(10)	3.6(9)	4.4(9)
98			2.3(8)	5.8(9)			1.3(9)	5.0(9)
210			6.0(8)					

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
28					2.8(10)	2.7(10)	2.7(10)	2.7(10)
95	3.2(10)	3.1(10)	3.0(10)	2.1(9)	4.0(9)	3.9(9)	3.9(9)	4.2(9)
98				9.2(8)				

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE XI

NO_2^- DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
48		1.3(6)*	2.8(8)		6.8(6)	4.6(9)	9.5(8)	
56			7.6(8)			3.0(9)	2.2(9)	
81					3.4(6)	2.3(9)	4.8(8)	
175				7.5(9)				7.9(9)
179			3.8(8)			1.5(9)	1.1(9)	
212				1.9(9)				1.5(9)
Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
48	6.1(7)							
56	1.5(8)	2.0(10)	1.9(10)		2.0(8)	5.6(9)	5.6(9)	5.5(9)
72						2.4(10)	2.5(10)	2.5(10)
175				3.0(9)				
179	7.6(8)	9.9(9)	9.3(9)		1.0(8)			

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE XII

O_2^- DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
47	2.2(8)*	1.3(10)				7.1(9)		
55		4.8(9)	7.6(9)			4.6(9)	5.7(9)	
64		4.5(9)						
77			3.8(9)					
79	1.1(8)	6.5(9)				3.5(9)		
95				3.9(9)	2.0(9)	1.2(10)		4.4(9)
96			1.25(10)	2.5(10)			1.4(10)	2.3(10)
173				4.3(9)				5.5(9)

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
95	3.2(10)	3.1(10)	3.0(10)		4.0(9)	3.9(9)	3.9(9)	4.2(9)
96				1.9(10)				
173				1.1(10)				

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE XIII

O_3^- DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.03(-1)s	1.22(1)s	1.12(3)s	Case III Rates at 1.02(-1)s	1.47(1)s	1.30(3)s
49	4.3(7)*	2.0(9)		2.0(7)	2.3(9)				
57	1.6(7)	5.3(9)		1.3(7)	5.2(9)				
80	2.2(7)			9.7(6)					
98			5.8(9)	1.2(7)		5.0(9)		1.7(8)	
174			1.7(10)			1.6(10)			1.3(10)
180		2.7(9)			2.6(9)				
208	1.4(7)			7.1(6)				1.1(8)	4.7(9)

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE XIV

NO_3^- POPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.03(-1)s	1.22(1)s	1.12(3)s	Case III Rates at 1.02(-1)s	1.47(1)s	1.30(3)s
173			4.3(9)		3.3(8)	5.5(9)			1.1(10)
174			1.7(10)		3.1(8)	1.6(10)			1.3(10)
175			7.5(9)			7.9(9)		1.2(9)	3.0(9)
211	1.2(6)*	1.2(9)			6.5(8)				
212				2.2(6)	2.5(8)		4.8(6)	7.8(8)	

Reaction Number	Case IV Rates at 1.30(-1)s	1.44(1)s	1.21(3)s
175		1.4(7)	3.4(8)

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE XV

O_2^+ DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
47	2.2(8)*	1.3(10)				7.1(9)		
48						4.6(9)		
64		4.5(9)						
79		6.5(9)				3.5(4)		
82				7.5(9)				7.3(9)
87			1.8(10)	1.5(10)	9.0(8)	5.4(9)	1.8(10)	1.6(10)
119	9.1(8)	6.0(9)	4.2(9)	5.5(9)	9.0(8)	5.2(9)	3.7(9)	5.3(9)
Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
82				7.0(9)				
87	2.9(10)	3.0(10)	3.0(10)	1.7(10)	3.1(10)	3.1(10)	3.1(10)	3.1(10)
119				6.0(9)				

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE XVI

NO^+ POPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
87			1.8(10)	1.5(10)	9.0(8)	5.4(9)	1.8(10)	1.6(10)
119	9.1(8)*	6.0(9)	4.2(9)	5.5(9)	9.0(8)	5.2(9)	3.7(9)	5.3(9)
190	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)	2.8(9)

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
87	2.9(10)	3.0(10)	3.0(10)	1.7(10)	3.1(10)	3.1(10)	3.1(10)	3.1(10)
119				6.0(9)				
190				2.8(9)				

*The quantity enclosed by parenthesis is the power to which ten is raised.

TABLE XVII

NO^+ DEPOPULATING RATES

(Units of cm^{-3} sec^{-1})

Reaction Number	Case I Rates at 1.08(-3)s	1.04(-1)s	1.06(1)s	1.00(3)s	Case II Rates at 1.08(-3)s	1.03(-1)s	1.22(1)s	1.12(3)s
32					6.6(6)			
55	2.5(7)*	4.8(9)	7.6(9)		2.8(7)	4.6(9)	5.7(9)	
56						3.0(9)		
57			5.3(9)				5.2(9)	
68	8.7(6)	1.7(9)	2.6(9)		9.5(6)	1.6(9)		
69				7.6(9)				7.8(9)
77	1.3(7)	2.4(9)	3.8(9)		1.4(7)	2.3(9)	2.8(9)	
170				1.5(10)				1.6(10)
179						1.5(9)		
180			2.7(9)				2.6(9)	
198	8.8(6)				1.0(7)			

Reaction Number	Case III Rates at 1.08(-3)s	1.02(-1)s	1.47(1)s	1.30(3)s	Case IV Rates at 1.06(-3)s	1.30(-1)s	1.44(1)s	1.21(3)s
56	1.5(8)	2.0(10)	1.9(10)			5.5(9)	5.6(9)	5.5(9)
69				7.9(9)				
170				1.6(10)				
179	7.6(7)	9.9(9)	9.3(6)					
198	6.2(7)							
199	1.3(8)				1.3(10)	2.6(10)	2.6(10)	2.6(10)

*The quantity enclosed by parenthesis is the power to which ten is raised.

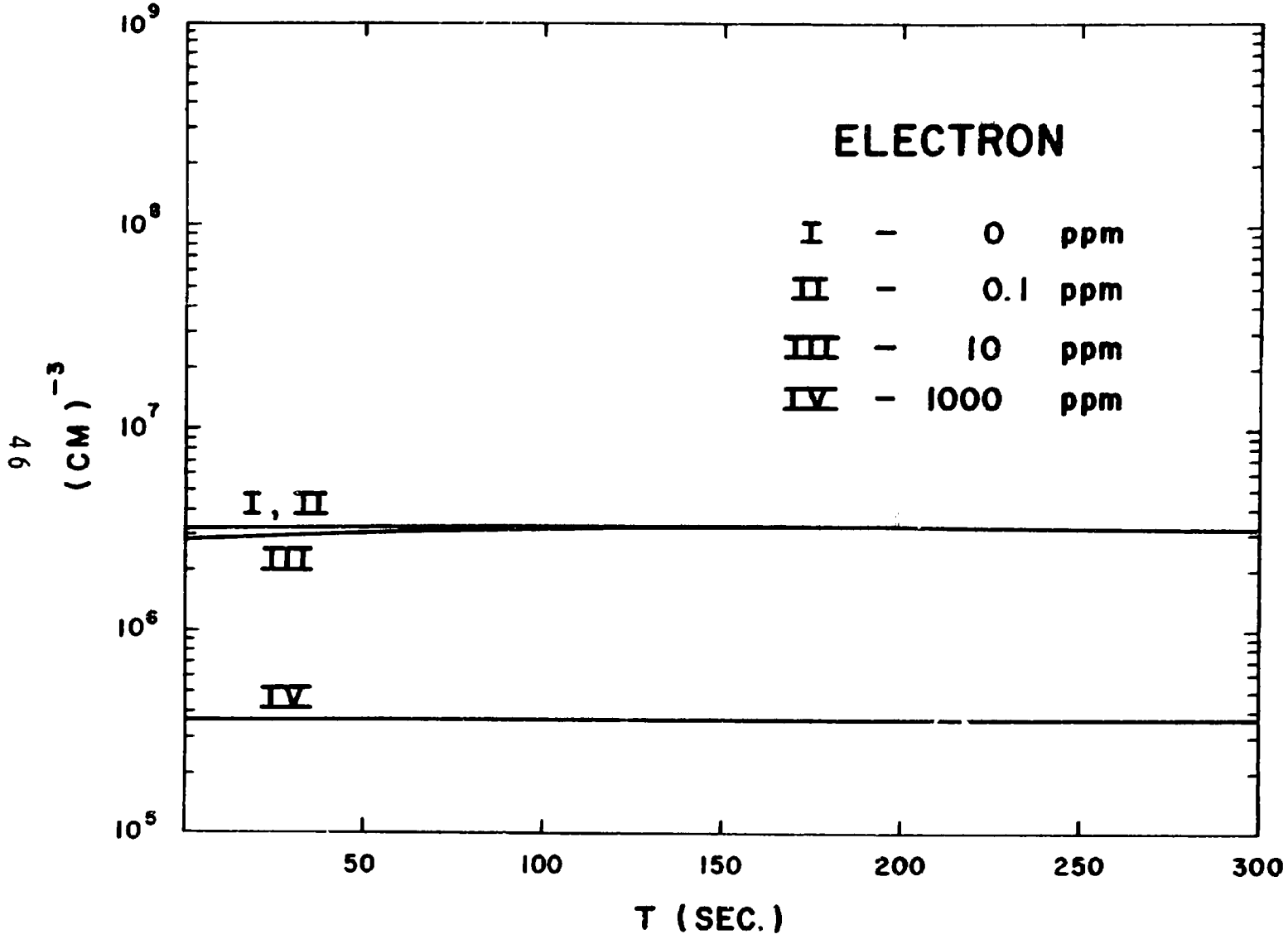

Figure 1. Electron Density Solutions During Interval 1 - 300 s

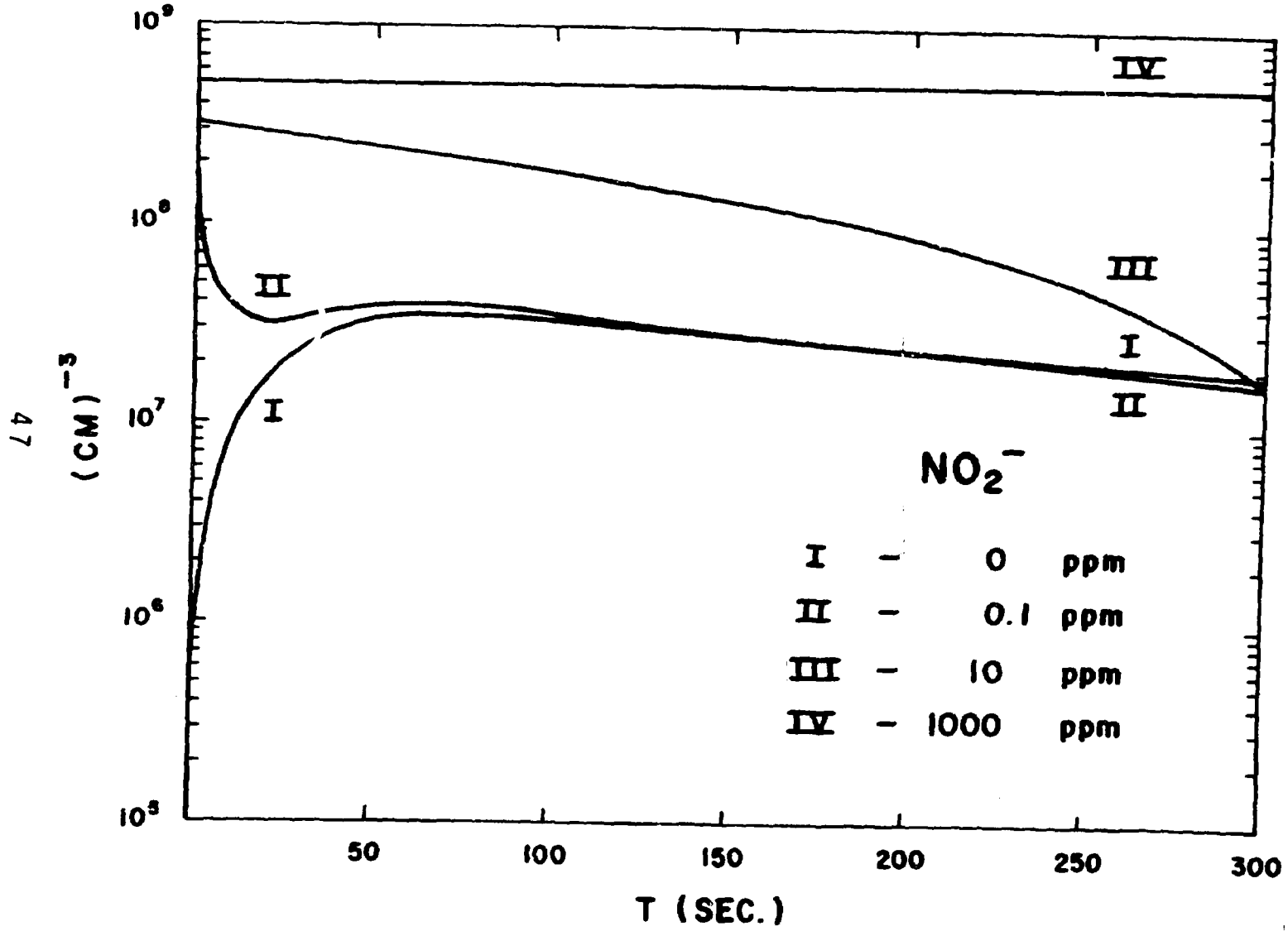

Figure 2. NO_2^- Density Solutions During Interval 1 - 300 s

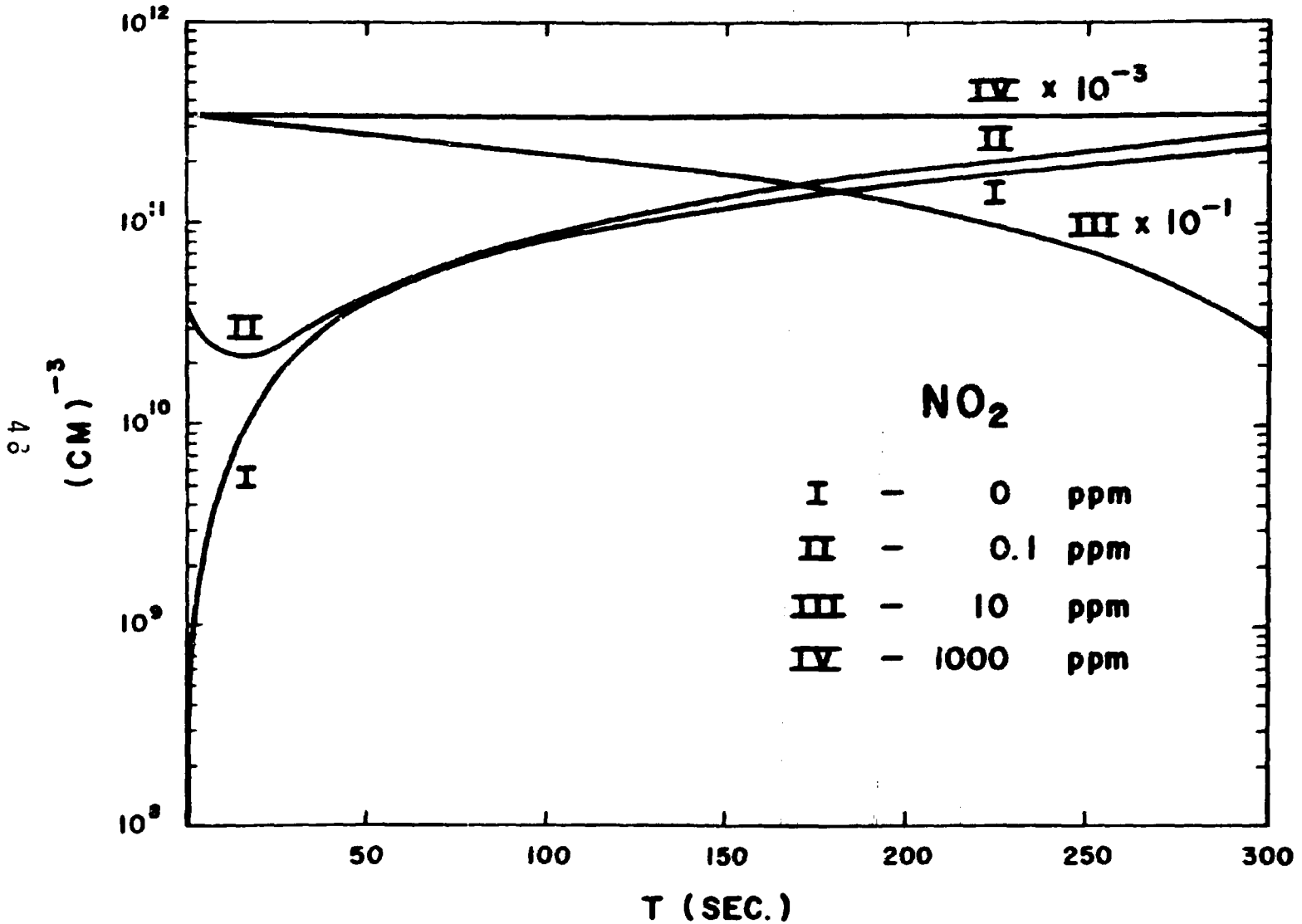

Figure 3. NO_2 Density Solutions During Interval 1 - 300 s

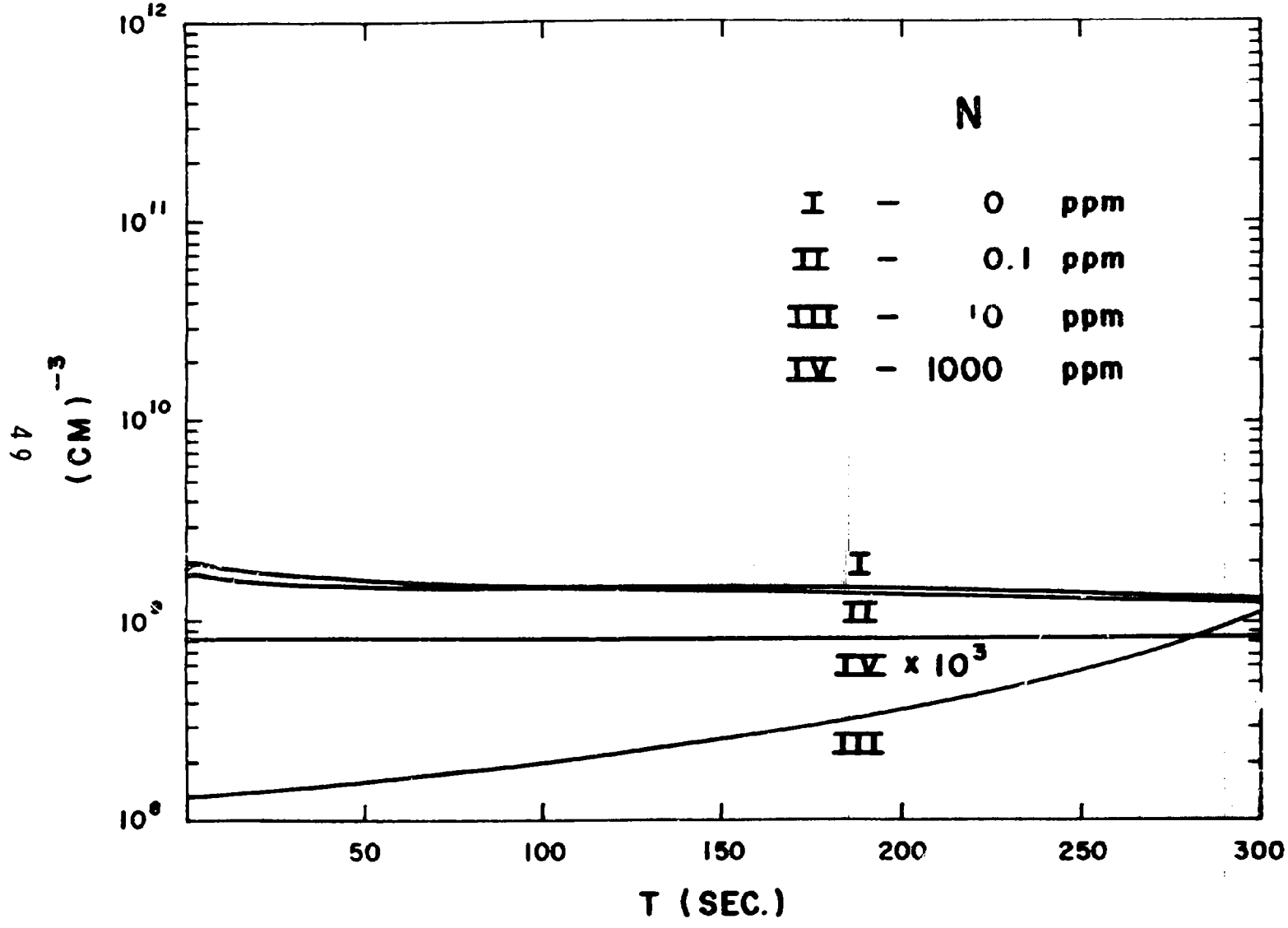

Figure 4. N Density Solutions During Interval 1 - 300 s

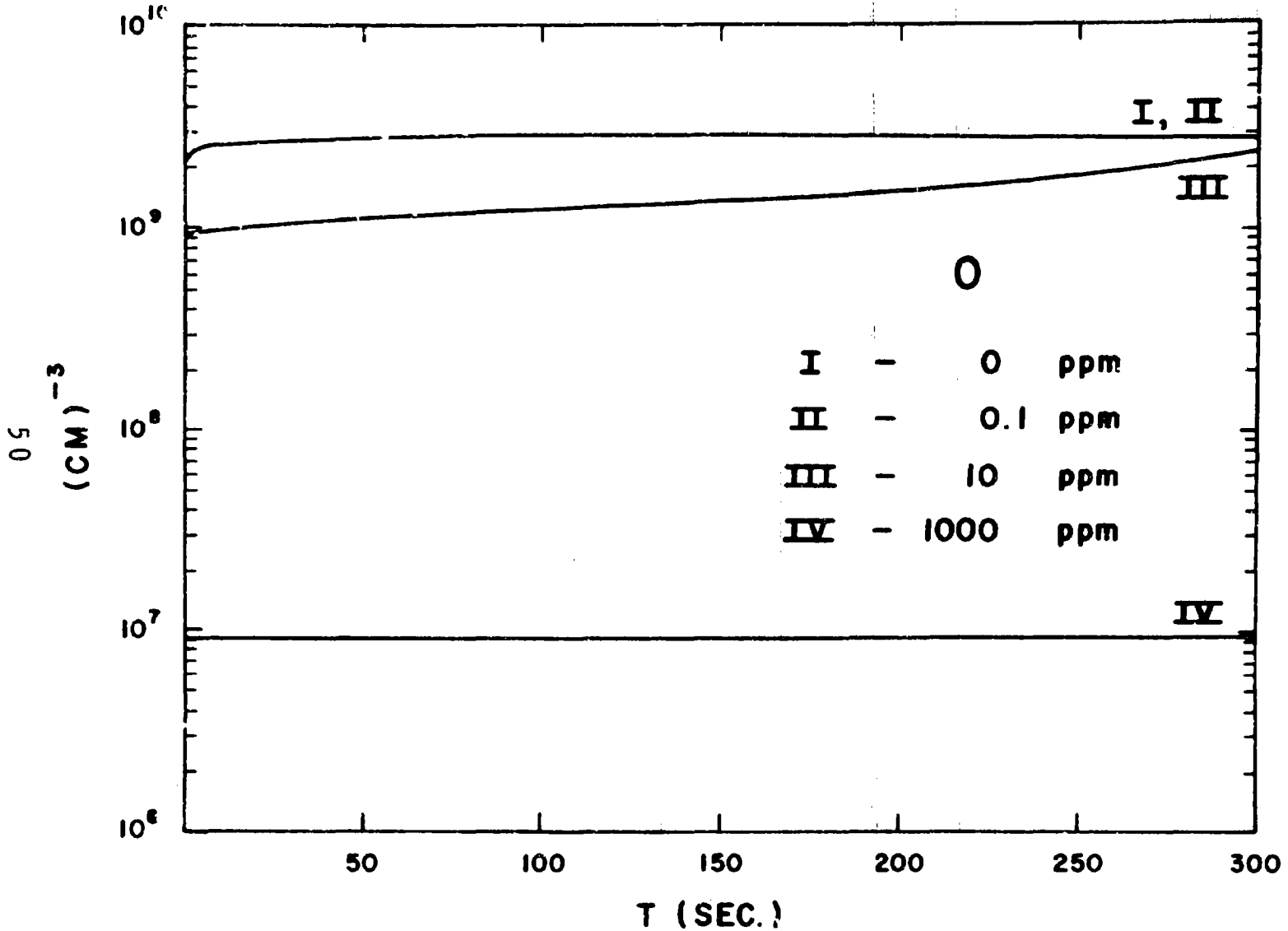

Figure 5. O Density Solutions During Interval 1 - 300 s

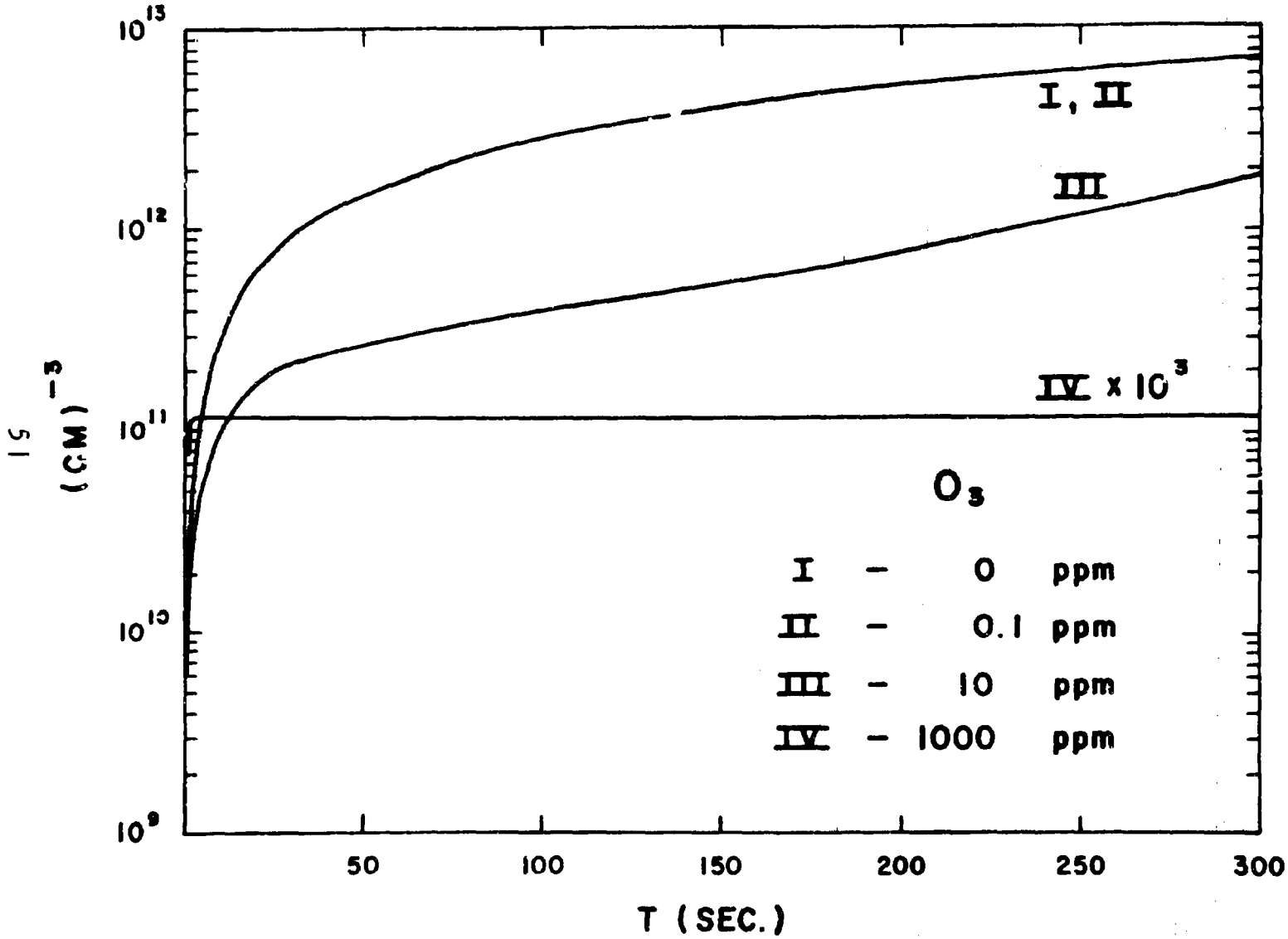

Figure 6. O_3 Density Solutions During Interval 1 - 300 s

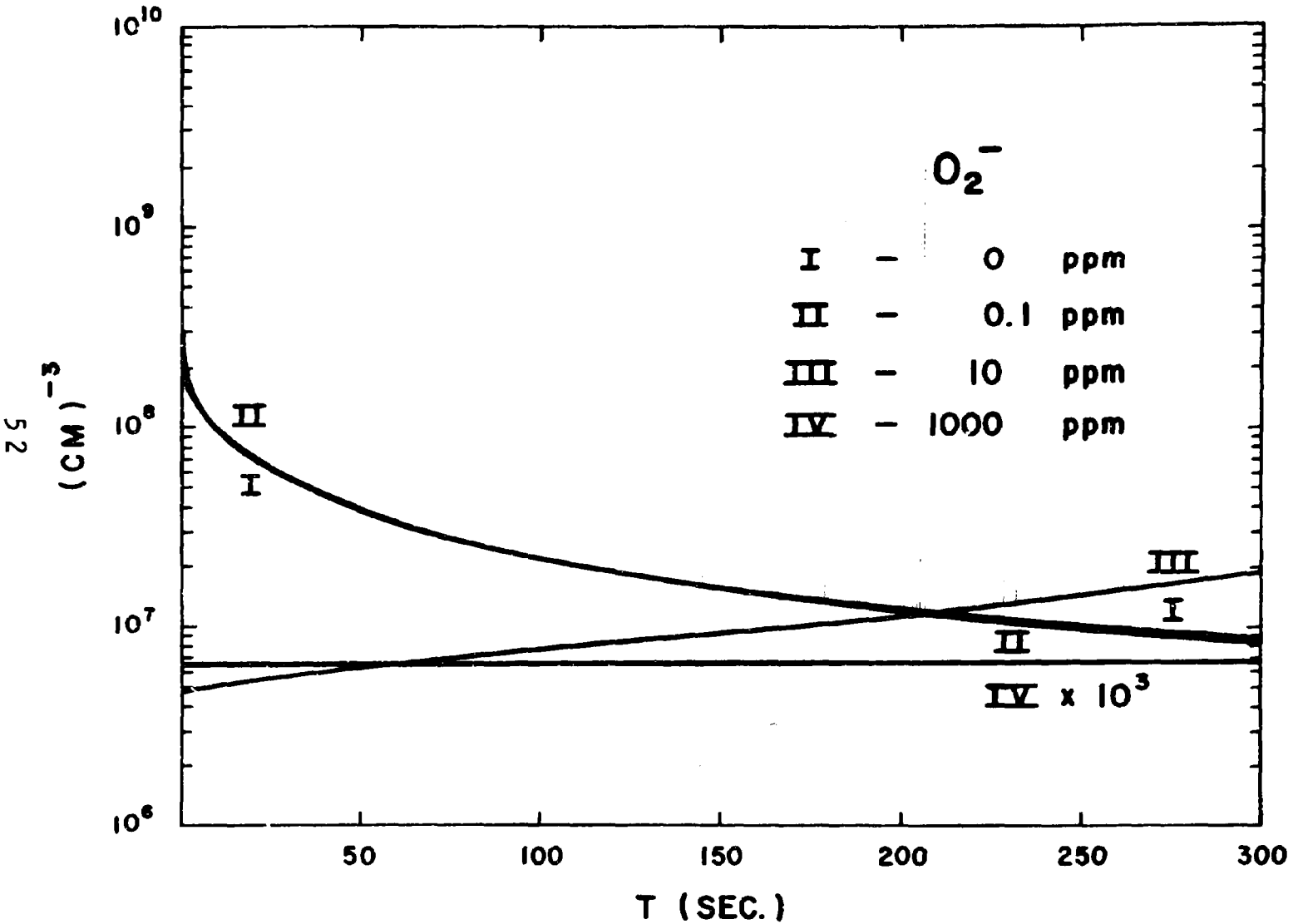

Figure 7. O_2^- Density Solutions During Interval 1 - 300 s

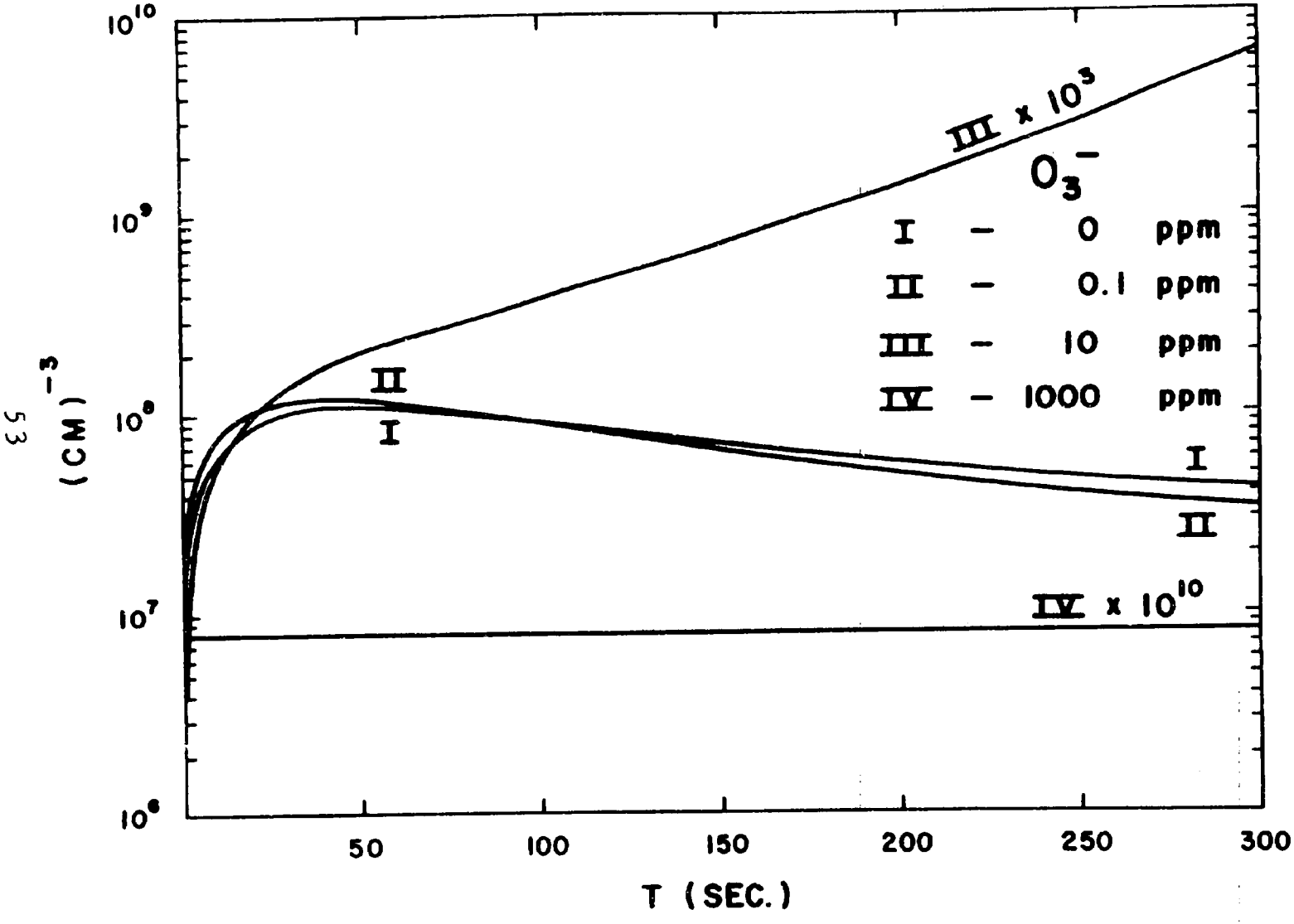

Figure 8. O_3^- Density Solutions During Interval 1 - 300 s

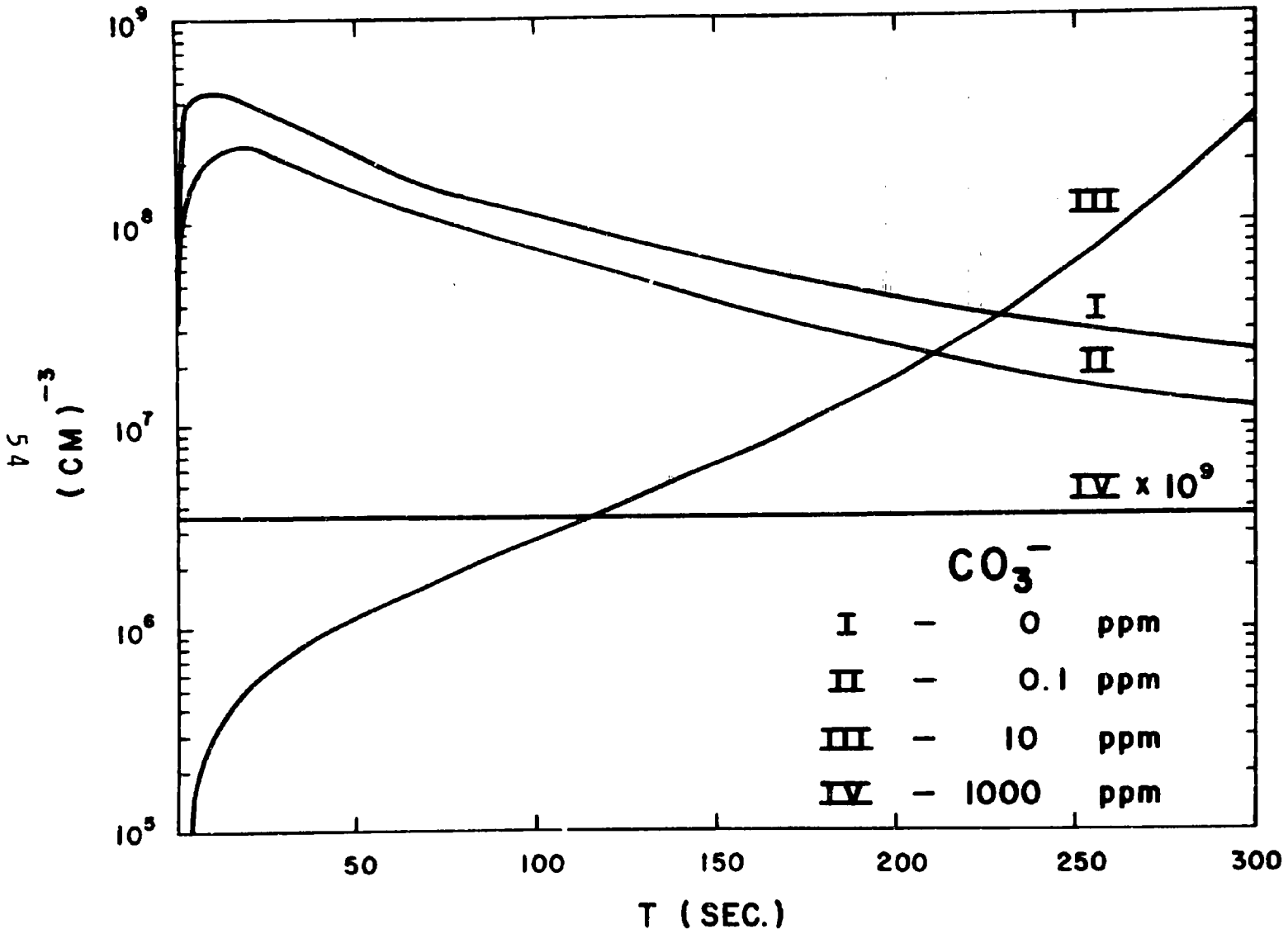

Figure 9. CO_3^- Density Solutions During Interval 1 - 300 s

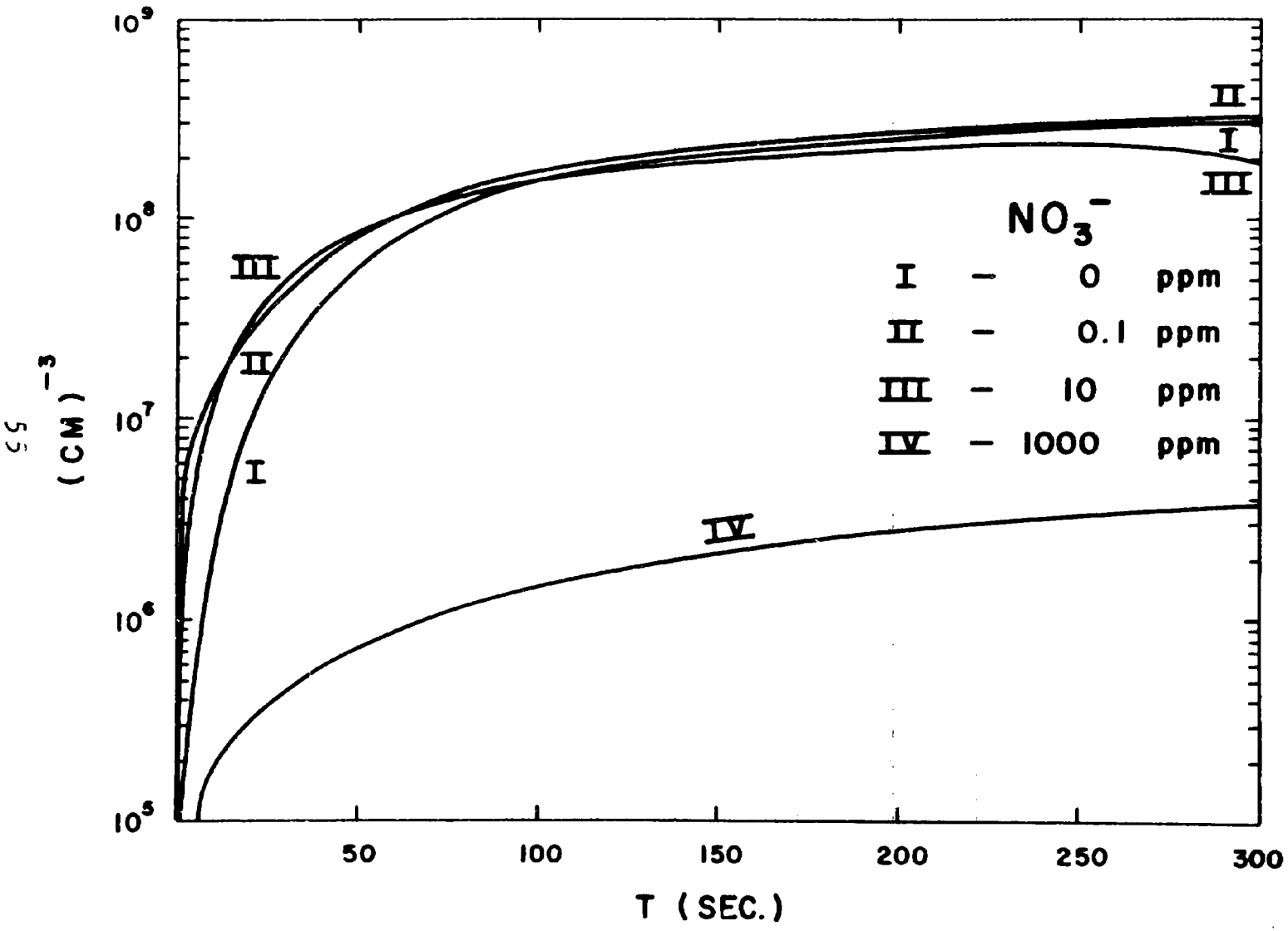

Figure 10. NO_3^- Density Solutions During Interval 1 - 300 s

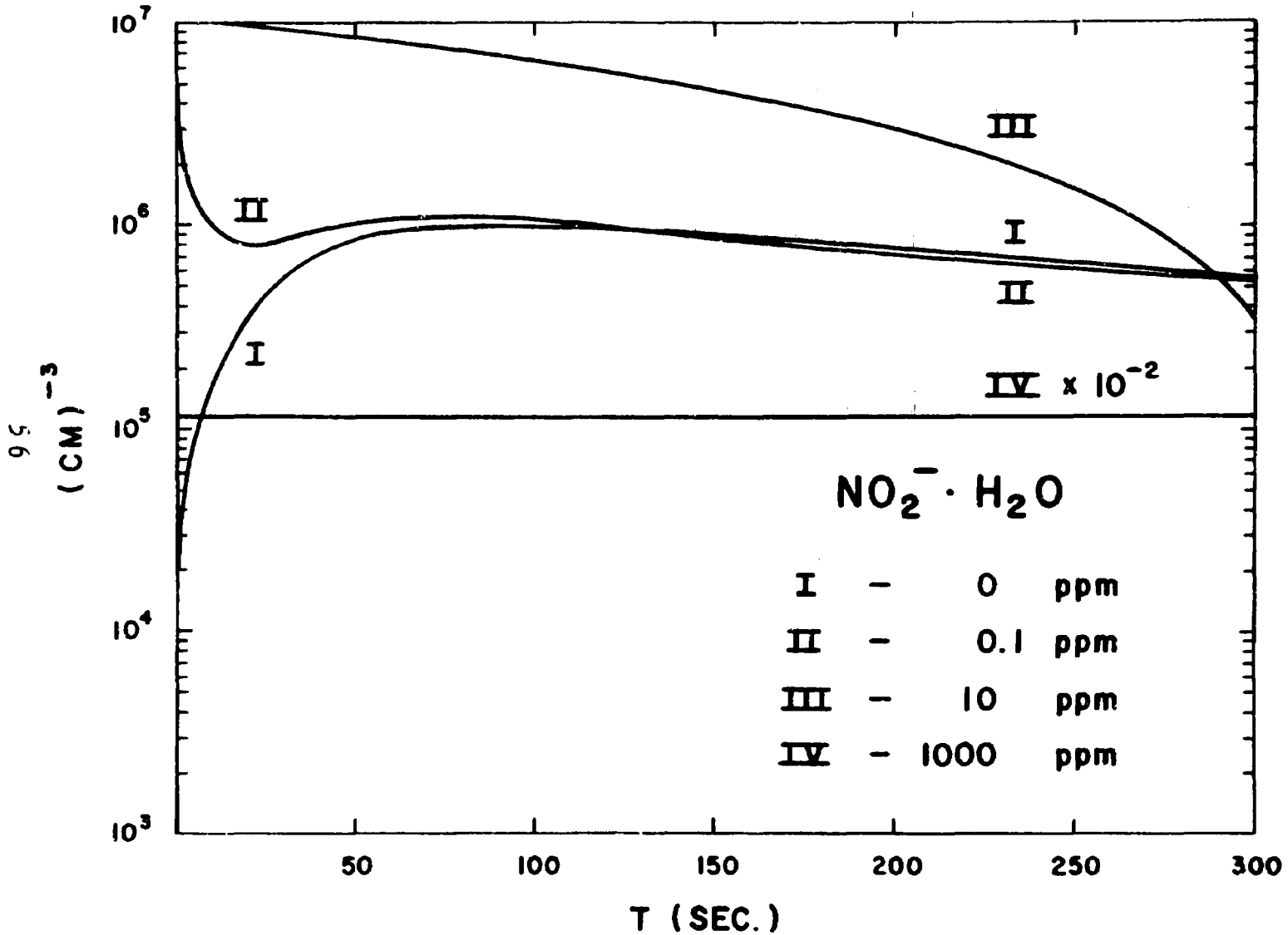

Figure 11. $NO_2^- \cdot H_2O$ Density Solutions During Interval 1 - 300 s

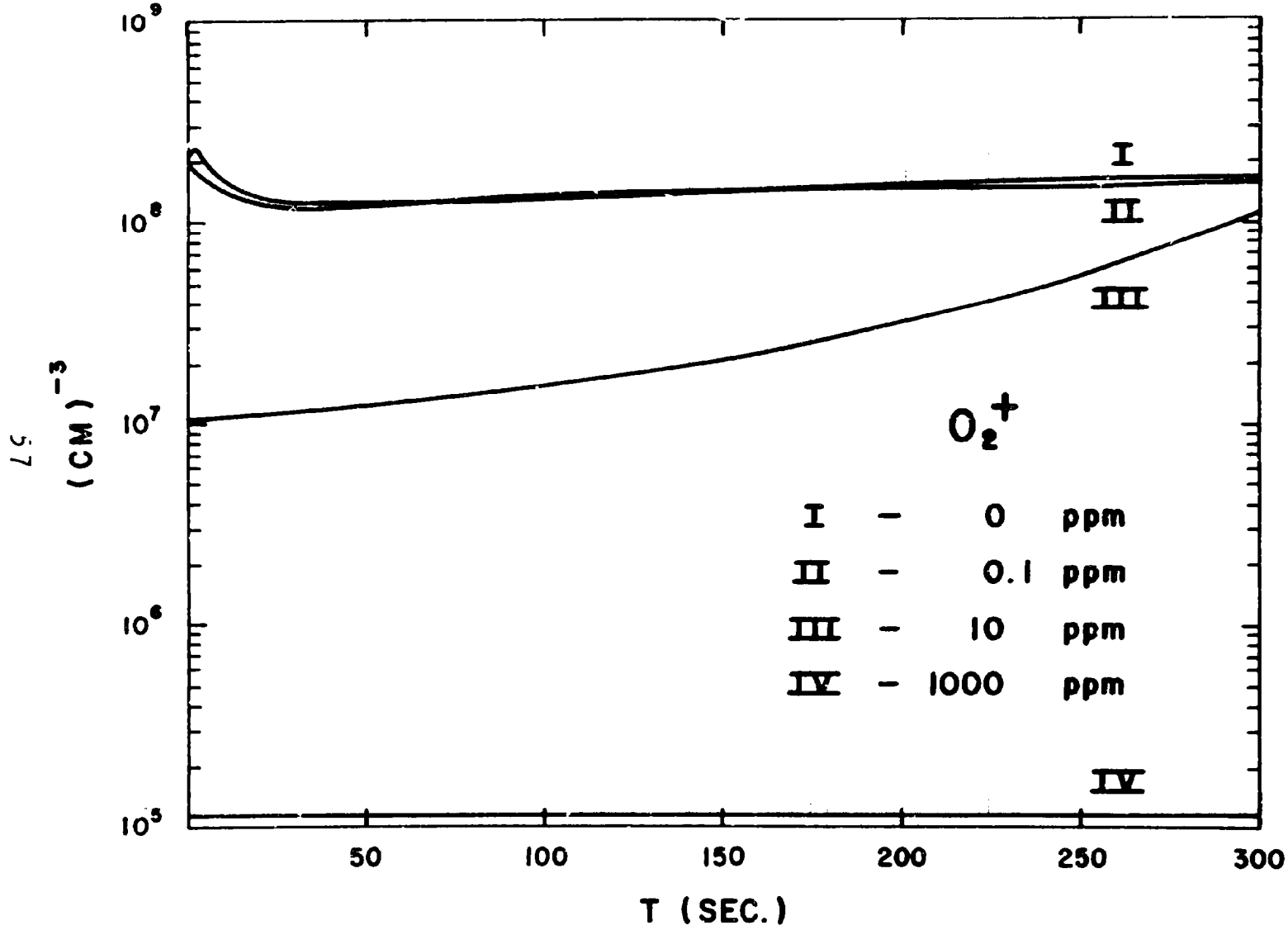

Figure 12. O_2^+ Density Solutions During Interval 1 - 300 s

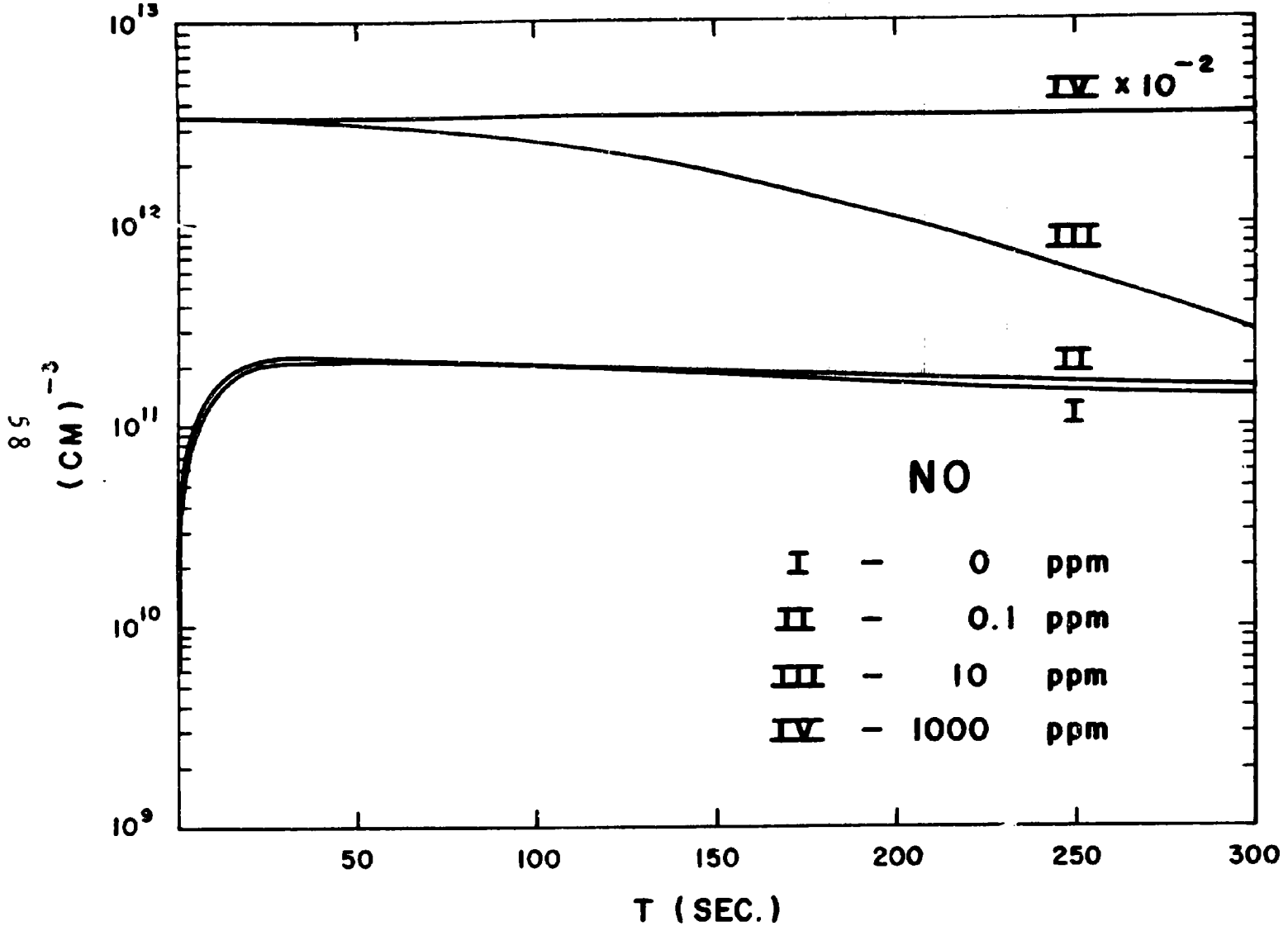

Figure 13. NO Density Solutions During Interval 1 - 300 s

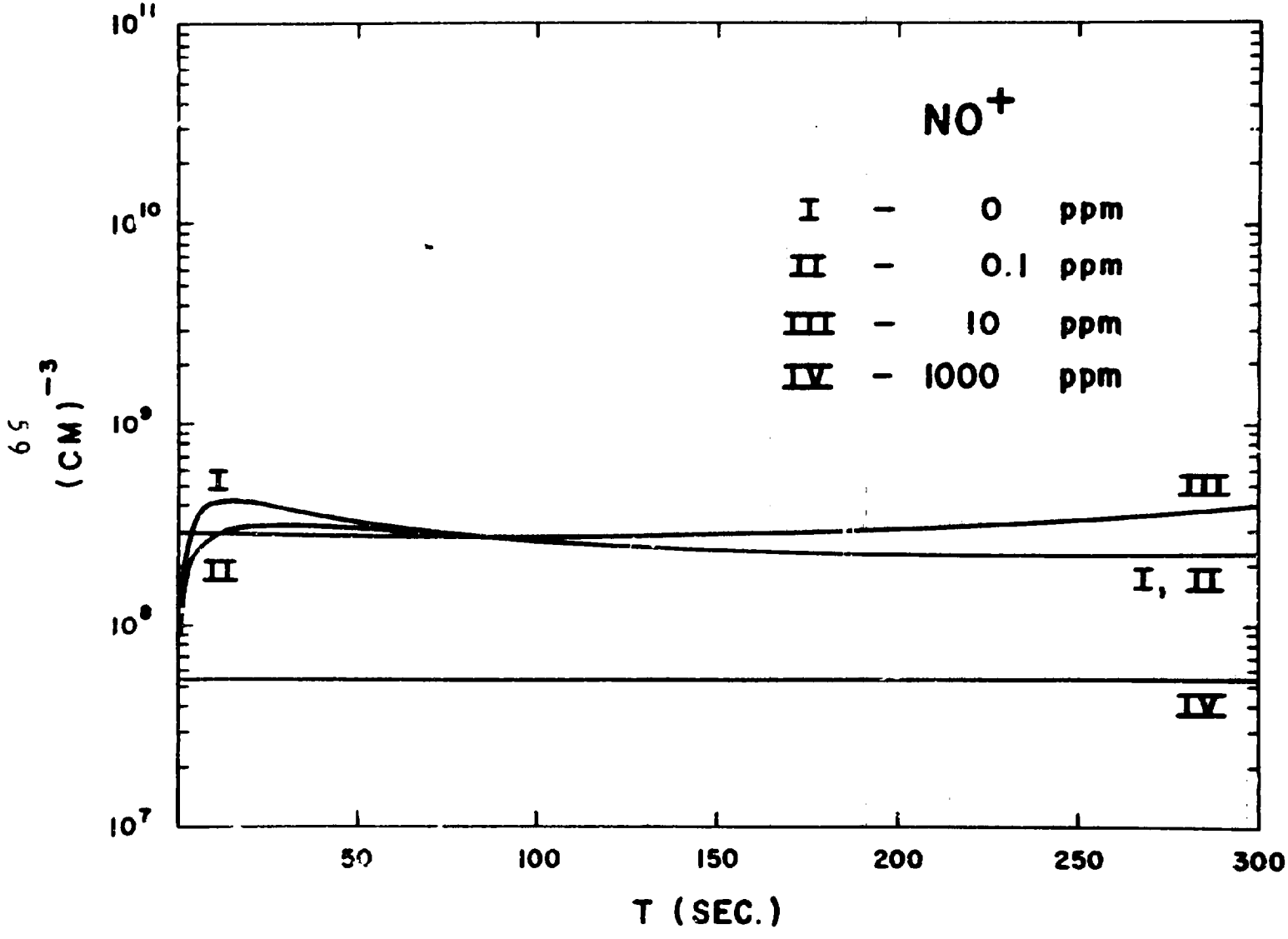

Figure 14. NO^+ Density Solutions During Interval 1 - 300 s

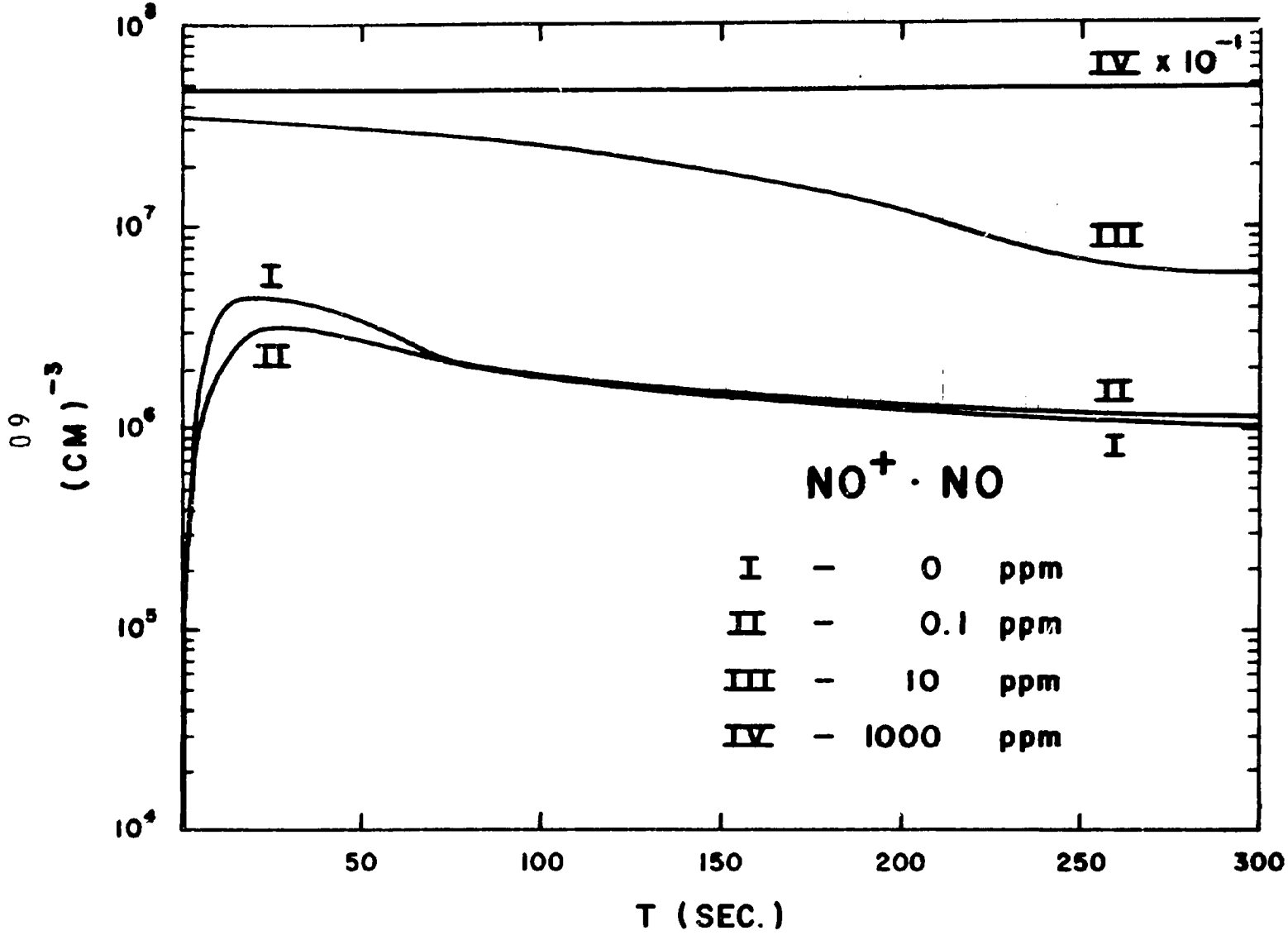

Figure 15. $NO^+ \cdot NO$ Density Solutions During Interval 1 - 300 s

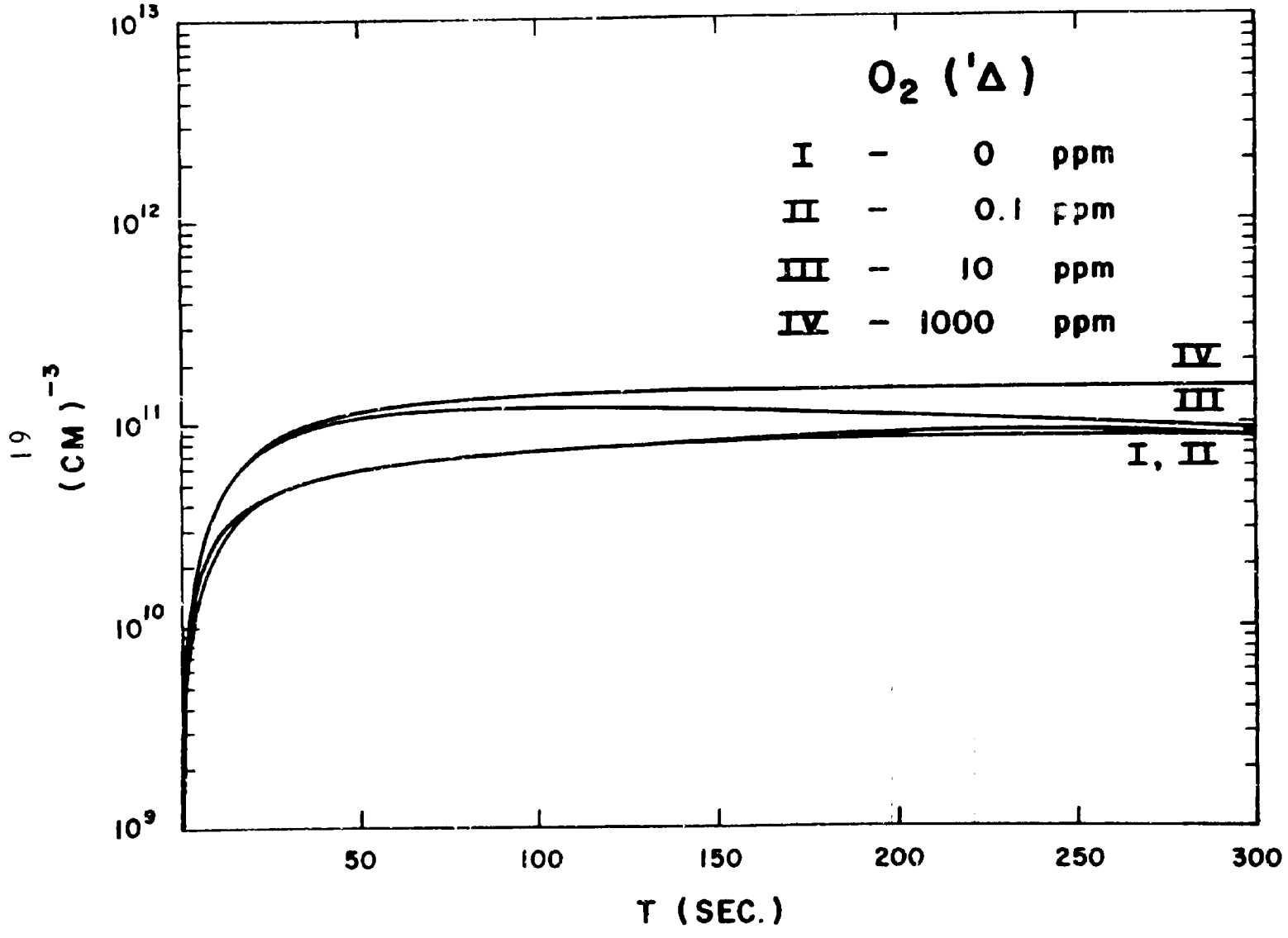

Figure 16. $O_2(^1\Delta)$ Density Solutions During Interval 1 - 300 s

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APPENDIX

REACTIONS AND RATE CONSTANTS AT 300 K

Reaction Number	Reaction	Rate Constant	Reaction Number	Reaction	Rate Constant
5.	$O_2^- + O_2 \rightarrow O_2 + e + O_2$	5.75(-19)	6.	$O_2^- + N_2 \rightarrow O_2 + e + N_2$	1.13(-19)
8.	$O^- + O \rightarrow O_2 + e$	1.40(-10)	9.	$O^- + O_2 \rightarrow O_3 + e$	5.00(-15)
10.	$O^- + N \rightarrow NO + e$	1.60(-10)	11.	$O^- + N_2 \rightarrow N_2O + e$	2.00(-19)
12.	$O^- + NO \rightarrow NO_2 + e$	2.00(-10)	14.	$O_2^- + N \rightarrow NO_2 + e$	3.00(-10)
15.	$O_2^- + O \rightarrow O_3 + e$	2.50(-10)	16.	$O + e \rightarrow O^- + h\nu$	1.30(-15)
17.	$O_2 + e \rightarrow O_2^- + h\nu$	2.00(-19)	18.	$NO_2 + e \rightarrow NO_2^- + h\nu$	1.00(-17)
19.	$O_3 + e \rightarrow O_3^- + h\nu$	1.00(-17)	20.	$O_3 + e \rightarrow O^- + O_2$	3.00(-12)
21.	$O_3 + e \rightarrow O_2^- + O$	3.78(-22)	22.	$O + e + O_2 \rightarrow O^- + O_2$	1.00(-31)
23.	$O + e + N_2 \rightarrow O^- + N_2$	1.00(-31)	24.	$O_2 + e + O_2 \rightarrow O_2^- + O_2$	1.89(-30)
25.	$O_2 + e + N_2 \rightarrow O_2^- + N_2$	1.00(-31)	26.	$O_2 + e + O \rightarrow O_2^- + O$	1.00(-31)
27.	$NO_2 + e + O_2 \rightarrow NO_2^- + O_2$	3.00(-28)	28.	$NO_2 + e + N_2 \rightarrow NO_2^- + N_2$	8.00(-28)
30.	$O_2^+ + e \rightarrow O + O$	2.20(- 7)	31.	$N_2^+ + e \rightarrow N + N$	2.80(- 7)
32.	$NO^+ + e \rightarrow N + O$	5.00(- 7)	33.	$O^+ + e + M \rightarrow O + M$	1.00(-26)
34.	$O_2^+ + e + M \rightarrow O_2 + M$	1.00(-26)	35.	$N_2^+ + e + M \rightarrow N_2 + M$	1.00(-26)
36.	$NO^+ + e + M \rightarrow NO + M$	1.00(-26)	37.	$NO^+ + e + M \rightarrow N + O + M$	1.00(-27)

Reaction Number	Reaction	Rate Constant	Reaction Number	Reaction	Rate Constant
38.	$O^+ + e \rightarrow O + h\nu$	3.50(-12)	39.	$O_2^+ + e \rightarrow O_2 + h\nu$	1.00(-12)
40.	$N_2^+ + e \rightarrow N_2 + h\nu$	1.00(-12)	41.	$NO^+ + e \rightarrow NO + h\nu$	1.00(-12)
42.	$O^- + O^+ \rightarrow O + O$	2.00(- 7)	43.	$O_2^- + O^+ \rightarrow O_2 + O$	2.00(- 7)
44.	$NO_2^- + O^+ \rightarrow NO_2 + O$	2.00(- 7)	45.	$O_3^- + O^+ \rightarrow O_3 + O$	2.00(- 7)
46.	$O^- + O_2^+ \rightarrow O + O_2$	2.00(- 7)	47.	$O_2^- + O_2^+ \rightarrow O_2 + O_2$	2.00(- 7)
48.	$NO_2^- + O_2^+ \rightarrow NO_2 + O_2$	2.00(- 7)	49.	$O_3^- + O_2^+ \rightarrow O_3 + O_2$	2.00(- 7)
50.	$O^- + N_2^+ \rightarrow O + N_2$	2.00(- 7)	51.	$O_2^- + N_2^+ \rightarrow O_2 + N_2$	2.00(- 7)
52.	$NO_2^- + N_2^+ \rightarrow NO_2 + N_2$	2.00(- 7)	53.	$O_3^- + N_2^+ \rightarrow O_3 + N_2$	2.00(- 7)
54.	$O^- + NO^+ \rightarrow O + NO$	2.00(- 7)	55.	$O_2^- + NO^+ \rightarrow O_2 + NO$	2.00(- 7)
56.	$NO_2^- + NO^+ \rightarrow NO_2 + NO$	2.00(- 7)	57.	$O_3^- + NO^+ \rightarrow O_3 + NO$	2.00(- 7)
58.	$O^- + O^+ + N \rightarrow O_2 + N$	2.00(-25)	59.	$O^- + O^+ + O_2 \rightarrow O_2 + O_2$	2.00(-25)
60.	$O^- + O^+ + N_2 \rightarrow O_2 + N_2$	2.00(-25)	61.	$O^- + O^+ + O \rightarrow O_2 + O$	2.00(-25)
62.	$O_2^- + O^+ + M \rightarrow O_3 + M$	2.00(-25)	63.	$O^- + O_2^+ + M \rightarrow O_3 + M$	2.00(-25)
64.	$O_2^- + O_2^+ + M \rightarrow O_2 + O_2 + M$	2.00(-25)	65.	$O^- + N_2^+ + M \rightarrow N_2O + M$	2.00(-25)
66.	$O_2^- + N_2^+ + M \rightarrow O_2 + N_2 + M$	2.00(-25)	67.	$O^- + NO^+ + M \rightarrow NO_2 + M$	2.00(-25)
68.	$O_2^- + NO^+ + M \rightarrow O_2 + NO + M$	2.00(-25)	69.	$NO_3^- + NO^+ \rightarrow NO_3 + N + O$	1.00(- 7)
70.	$O_2^- + NO^+ \cdot NO \rightarrow O_2 + NO + NO$	1.00(- 7)	71.	$O_3^- + NO^+ \cdot NO \rightarrow O_3 + NO + NO$	1.00(- 7)

Reaction Number	Reaction	Rate Constant	Reaction Number	Reaction	Rate Constant
72.	$NO_2^- + NO^+ \cdot NO \rightarrow NO_2 + NO + NO$	1.00(- 7)	73.	$NO_3^- + NO^+ \cdot NO \rightarrow NO_3 + NO + NO$	1.00(- 7)
74.	$O_2^- + NO^+ \cdot H_2O \rightarrow O_2 + NO + H_2O$	1.00(- 7)	75.	$O_3^- + NO^+ \cdot H_2O \rightarrow O_3 + NO + H_2O$	1.00(- 7)
76.	$NO_2^- + NO^+ \cdot H_2O \rightarrow NO_2 + NO + H_2O$	1.00(- 7)	77.	$O_2^- + NO^+ \rightarrow O_2 + N + O$	1.00(- 7)
78.	$NO_3^- + NO^+ \cdot H_2O \rightarrow NO_3 + NO + H_2O$	1.00(- 7)	79.	$O_2^- + O_2^+ \rightarrow O_2 + O + O$	1.00(- 7)
80.	$O_3^- + O_2^+ \rightarrow O_3 + O + O$	1.00(- 7)	81.	$NO_2^- + O_2^+ \rightarrow NO_2 + O + O$	1.00(- 7)
82.	$NO_3^- + O_2^+ \rightarrow NO_3 + O + O$	1.00(- 7)	83.	$O^+ + O_2 \rightarrow O + O_2^+$	2.00(-11)
84.	$O^+ + NO \rightarrow O + NO^+$	2.40(-11)	87.	$O_2^+ + NO \rightarrow O_2 + NO^+$	8.00(-10)
88.	$N_2^+ + O \rightarrow N_2 + O^+$	1.00(-12)	89.	$N_2^+ + O_2 \rightarrow N_2 + O_2^+$	2.00(-10)
90.	$N_2^+ + N \rightarrow N_2 + N^+$	1.00(-12)	91.	$N_2^+ + NO \rightarrow N_2 + NO^+$	5.00(-10)
92.	$O^- + NO_2 \rightarrow O + NO_2^-$	1.00(- 9)	93.	$O^- + O_3 \rightarrow O + O_3^-$	5.30(-10)
94.	$O_2^- + O \rightarrow O_2 + O^-$	1.00(-11)	95.	$O_2^- + NO_2 \rightarrow O_2 + NO_2^-$	1.80(- 9)
96.	$O_2^- + O_3 \rightarrow O_2 + O_3^-$	4.00(-10)	98.	$O_3^- + NO_2 \rightarrow O_3 + NO_2^-$	7.00(-10)
99.	$O^+ + O \rightarrow O_2^+ + h\nu$	1.00(-17)	100.	$O^+ + N \rightarrow NO^+ + h\nu$	1.00(-18)
106.	$O^- + O_2 \rightarrow O_3^- + h\nu$	1.00(-17)	107.	$O^+ + O + M \rightarrow O_2^+ + M$	1.00(-29)
108.	$O^+ + N + M \rightarrow NO^+ + M$	1.00(-29)	114.	$O^- + NO + M \rightarrow NO_2^- + M$	1.00(-29)
115.	$O_2^- + N + M \rightarrow NO_2^- + M$	1.00(-29)	116.	$O^+ + N_2 \rightarrow NO^+ + N$	1.00(-12)
117.	$O^+ + NO \rightarrow O_2^+ + N$	3.00(-12)	119.	$O_2^+ + N_2 \rightarrow NO^+ + NO$	1.00(-16)

Reaction Number	Reaction	Rate Constant	Reaction Number	Reaction	Rate Constant
120.	$O_2^+ + N \rightarrow NO^+ + O$	1.80(-10)	121.	$O_2^+ + NO_2 \rightarrow NO^+ + O_3$	1.00(-11)
122.	$N_2^+ + O \rightarrow NO^+ + N$	2.50(-10)	123.	$N_2^+ + O_2 \rightarrow NO^+ + NO$	1.00(-17)
124.	$O^- + O_2 + O_2 \rightarrow O_3^- + O_2$	1.00(-29)	125.	$O_2^- + O_2 + N_2 \rightarrow NO_2^- + NO_2$	5.78(-42)
126.	$O_3^- + N_2 \rightarrow NO_2^- + NO$	1.00(-20)	129.	$N + O \rightarrow NO + h\nu$	2.00(-17)
131.	$O + NO \rightarrow NO_2 + h\nu$	6.20(-17)	132.	$N + N \rightarrow N_2 + h\nu$	1.00(-17)
135.	$O + O + O_2 \rightarrow O_2 + O_2$	3.00(-33)	136.	$O + O + O \rightarrow O_2 + O$	3.00(-33)
137.	$O + O + N_2 \rightarrow O_2 + N_2$	3.00(-33)	138.	$O + O_2 + O_2 \rightarrow O_3 + O_2$	5.50(-34)
139.	$O + O_2 + N_2 \rightarrow O_3 + N_2$	5.50(-34)	140.	$O + O_2 + O \rightarrow O_3 + O$	5.50(-34)
141.	$N + O + M \rightarrow NO + M$	1.10(-32)	142.	$O + N_2 + M \rightarrow N_2O + M$	1.39(-45)
143.	$O + NO + O_2 \rightarrow NO_2 + O_2$	1.00(-31)	144.	$O + NO + N_2 \rightarrow NO_2 + N_2$	1.00(-31)
145.	$N + N + M \rightarrow N_2 + M$	5.00(-33)	147.	$N + NO + M \rightarrow N_2O + M$	3.57(-36)
148.	$NO + O_2 + NO \rightarrow NO_2 + NO_2$	1.62(-46)	149.	$O + N_2 \rightarrow NO + N$	1.36(-65)
150.	$O + NO \rightarrow O_2 + N$	6.73(-41)	151.	$O + NO_2 \rightarrow NO + O_2$	4.48(-12)
152.	$O + N_2O \rightarrow NO + NO$	8.11(-31)	153.	$O + N_2O \rightarrow O_2 + N_2$	2.70(-31)
154.	$O + O_3 \rightarrow O_2 + O_2$	9.43(-15)	155.	$N + O_2 \rightarrow NO + O$	8.60(-17)
156.	$N + NO \rightarrow N_2 + O$	2.20(-11)	157.	$N + NO_2 \rightarrow N_2 + O_2$	1.50(-11)
158.	$N + NO_2 \rightarrow NO + NO$	3.00(-12)	159.	$N + NO_2 \rightarrow N_2O + O$	1.50(-13)

Reaction Number	Reaction	Rate Constant	Reaction Number	Reaction	Rate Constant
160.	$NO + O_3 \rightarrow NO_2 + O_2$	1.25(-14)	167.	$O_3^- + O \rightarrow O_2^- + O_2$	1.00(-10)
168.	$O_3^- + NO \rightarrow NO_3^- + O$	1.00(-11)	170.	$NO_3^- + NO^+ \rightarrow NO_3 + NO$	2.00(- 7)
171.	$O_3^- + NO_2 \rightarrow NO_3^- + O_2$	2.00(-11)	172.	$NO_2 + O_3 \rightarrow NO_3 + O_2$	7.00(-17)
173.	$O_2^- + NO_3 \rightarrow O_2 + NO_3^-$	5.00(-10)	174.	$O_3^- + NO_3 \rightarrow O_3 + NO_3^-$	5.00(-10)
175.	$NO_2^- + NO_3 \rightarrow NO_2 + NO_3^-$	5.00(-10)	176.	$O_2^- + N_2^+ \rightarrow O_2 + N + N$	1.00(- 7)
177.	$NO_2^- + N_2^+ \rightarrow NO_2 + N + N$	1.00(- 7)	178.	$O_3^- + N_2^+ \rightarrow O_3 + N + N$	1.00(- 7)
179.	$NO_2^- + NO^+ \rightarrow NO_2 + N + O$	1.00(- 7)	180.	$O_3^- + NO^+ \rightarrow O_3 + N + O$	1.00(- 7)
181.	$N^+ + e + M \rightarrow N + M$	1.00(-26)	182.	$N^+ + e \rightarrow N + h\nu$	3.50(-12)
183.	$N^+ + O^- \rightarrow N + O$	2.00(- 7)	184.	$N^+ + O \rightarrow N + O^+$	1.00(-12)
185.	$N^+ + O_2 \rightarrow N + O_2^+$	5.00(-10)	186.	$N^+ + NO \rightarrow N + NO^+$	8.00(-10)
189.	$N^+ + O_2 \rightarrow O^+ + NO$	1.00(-12)	190.	$N^+ + O_2 \rightarrow NO^+ + O$	5.00(-10)
191.	$N^+ + NO \rightarrow O^+ + N_2$	1.00(-12)	192.	$N^+ + NO \rightarrow N_2^+ + O$	3.00(-12)
194.	$N^+ + O \rightarrow NO^+ + h\nu$	1.00(-17)	195.	$N^+ + N \rightarrow N_2^+ + h\nu$	3.00(-17)
196.	$N^+ + O + M \rightarrow NO^+ + M$	1.00(-29)	197.	$N^+ + N + M \rightarrow N_2^+ + M$	1.00(-29)
198.	$NO^+ + H_2O + M \rightarrow NO^+ \cdot H_2O + M$	2.00(-28)	199.	$NO^+ + NO + M \rightarrow NO^+ \cdot NO + M$	4.00(-30)
200.	$O_2^- + O_2^+ \rightarrow O_2 + O_2(^1\ell)$	1.00(- 8)	201.	$O_2^- + O_2(^1\Delta) \rightarrow O_2 + e + O_2$	1.00(-9)
202.	$O^- + O_2(^1\Delta) \rightarrow O_2^- + O$	1.00(- 9)	203.	$O^- + O_2(^1\Delta) \rightarrow O_3 + e$	1.00(-10)

Reaction Number	Reaction	Rate Constant	Reaction Number	Reaction	Rate Constant
204.	$O_3 + O_2(^1\Delta) \rightarrow O + O_2 + O_2$	1.87(-15)	205.	$O_2(^1\Delta) + M \rightarrow O_2 + M$	1.00(-19)
206.	$O_2(^1\Delta) \rightarrow O_2 + h\nu$	2.58(- 4)	207.	$O_2(^1\Delta) + N \rightarrow NO + O$	3.00(-12)
208.	$O_3^- + CO_2 \rightarrow O_2 + CO_3^-$	4.00(-10)	209.	$CO_3^- + O \rightarrow CO_2 + O_2^-$	8.00(-11)
210.	$CO_3^- + NO \rightarrow CO_2 + NO_2^-$	9.00(-12)	211.	$CO_3^- + NO_2 \rightarrow CO_2 + NO_3^-$	8.00(-11)
212.	$NO_2^- + O_3 \rightarrow O_2 + NO_3^-$	1.80(-11)	213.	$NO^+ \cdot NO + e \rightarrow NO + NO$	1.70(- 6)
214.	$NO^+ \cdot H_2O + e \rightarrow NO + H_2O$	1.00(- 6)	215.	$NO_2^- + H_2O + M \rightarrow NO_2^- \cdot H_2O + M$	1.00(-28)
216.	$NO_2^- \cdot H_2O + NO^+ \rightarrow NO_2 + H_2O + NO$	1.00(- 7)	217.	$NO_2^- \cdot H_2O + O_2^+ \rightarrow NO_2 + H_2O + O_2$	1.00(- 7)
218.	$NO_2^- \cdot H_2O + NO^+ \cdot H_2O \rightarrow NO_2 + 2H_2O + NO$	1.00(- 7)	219.	$NO_2^- \cdot H_2O + NO^+ \cdot NO \rightarrow NO_2 + H_2O + 2NO$	1.00(- 7)

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13. ABSTRACT

Computer solutions to 24 time-rate-of-change equations have been obtained for air-like discharges attainable in a laboratory facility designed for the study of reactions of ionospheric importance. The manner in which the solutions are affected by initial number densities of CO_2, NO, NO_2, and N_2O, corresponding to impurity levels of 0, 0.1, 10, and 1000 ppm, is presented. The effects of principal reactions on the number densities of detectable species are discussed. For the conditions specified in the computer program, the initial NO_2 density greatly affects the negative ion densities and the initial NO density greatly affects the observable positive ion densities.

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